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# COLLOIDAL LIGNIN PARTICLES IN WOOD ADHESIVES

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Fibre and Polymer Technology

Master's thesis for the degree of Master of Science in Technology
submitted for inspection, Espoo, 16th of June, 2020.

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**Abstract of master's thesis**

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|---|---|
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| **Title of thesis** | COLLOIDAL LIGNIN PARTICLES IN WOOD ADHESIVES |
| **Degree Programme** | Degree Programme of Chemical, Biochemical and Materials Engineering |
| **Major** | Fibre and Polymer Engineering |
| **Thesis supervisor** | Professor Lauri Rautkari |
| **Thesis advisor(s) / Thesis examiner(s)** | D.Sc Kalle Lintinen |
| **Date** 16.06.2020 | **Number of pages** 42 + 7 **Language** English |

## Abstract

Replacing environmentally toxic materials with greener and naturally safe solutions has gained increasing interest among scientists. One area of interest has been the possibility to replace part of the toxic compounds in wood adhesives with more environmentally friendly solutions. The aim of this master's thesis was to test how colloidal lignin particles could be used in wood adhesives both in wet and dry conditions. To achieve this goal, various batches of adhesives were manufactured, and finally the adhesives were tested with Automated bonding evaluation system (ABES) to determine the shear strengths of the glue joints. Adhesives had several different ratios of solid contents and were either combinations of CLP:PDADMAC+TONFC, CLP+CLP:PDADMAC or Dirty Lignoboost+PF. The ABES tests had various parameters, including temperature and adhesive dosage.

Based on the ABES tests, all adhesives had weaker shear strength properties compared to PF reference. However, the TONFC+CLP:PDADMAC adhesives had weaker glue joint strength in overall compared to CLP+CLP:PDADMAC samples. The combination of Dirty Lignoboost and PF had most promising results of all adhesives. By substituting either 20% or 40% of the PF with Dirty Lignoboost, resulted as higher shear strength results in wet samples compared to PF reference.

The results indicate in overall that although PF reference has higher shear strength compared to other tested adhesives, there is room for further investigation of as an example whether the adhesive bonding could be improved in wet samples. In addition, it should be studied if the dry content ratios of the adhesives could be increased without making the adhesives too solid for application with pipette.

**Keywords** CLP, Wood adhesives, ABES

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**Diplomityön tiivistelmä**

**Tekijä** Niko Tuominen

**Työn nimi** Kolloidaaliset ligniinipartikkelit puuliimoissa

**Koulutusohjelma** Biotuotteiden ja biotekniikan laitos

**Pääaine** Kuitu- ja polymeeritekniikka

**Työn valvoja** Professori Lauri Rautkari

**Työn ohjaaja(t)/Työn tarkastaja(t)** TkT Kalle Lintinen

**Päivämäärä** 16.06.2020 **Sivumäärä** 42 + 7 **Kieli** Englanti

## Tiivistelmä

Ympäristölle myrkyllisten materiaalien korvaaminen vihreämmillä ja luonnollisesti turvallisilla ratkaisuilla on saanut yhä enemmän kiinnostusta tutkijoiden keskuudessa. Eräs mielenkiinnon kohteeksi joutunut aihealue on ollut mahdollisuus korvata osa puuliimoissa olevista myrkyllisistä yhdisteistä ympäristöystävällisemmillä ratkaisuilla. Tämän opinnäytetyön tarkoituksena oli testata, kuinka kolloidaalisia ligniinipartikkeleita voidaan käyttää puuliimoissa sekä märissä että kuivissa olosuhteissa. Tämän tavoitteen saavuttamiseksi valmistettiin erilaisia liimaeriä, ja lopuksi liimat testattiin ABES-liimasaumatestillä liimojen liitosten leikkauslujuuksien määrittämiseksi. Liimoilla oli useita erilaisia kiinteiden pitoisuuksien suhteita ja ne olivat joko CLP:PDADMAC + TONFC, CLP + CLP:PDADMAC tai Dirty Lignoboost + PF yhdistelmiä. ABES-testeillä oli erilaisia parametrejä, mukaan lukien lämpötila ja liima-annos.

ABES-testien perusteella kaikilla liimoilla oli heikommat leikkauslujuusominaisuudet verrattuna PF-referenssiin. TONFC + CLP:PDADMAC-liimoilla oli kuitenkin yleisesti ottaen heikompi liiman liitoslujuus verrattuna CLP + CLP:PDADMAC-näytteisiin. Dirty Lignoboostin ja PF: n yhdistelmällä oli lupaavimmat tulokset kaikista liimoista. Korvaamalla joko 20 % tai 40 % PF: stä Dirty Lignoboostilla, seurauksena oli suurempi leikkauslujuus märissä näytteissä verrattuna PF-referenssiin.

Tulokset osoittavat kaiken kaikkiaan, että vaikka PF-referenssillä on suurempi leikkauslujuus verrattuna muihin testattuihin liimoihin, on tilaa jatkotutkimuksille esimerkkinä siitä, voidaanko liiman sitoutumista parantaa märissä näytteissä. Lisäksi on tutkittava, voidaanko liimojen kuivapitoisuuksia nostaa tekemättä liimoista liian kiinteitä pipetillä levittämistä varten.

**Avainsanat** CLP, Puuliimat, ABES

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**LIST OF NOMENCLATURE**

## LIST OF APPENDICES



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| | |
|---|---|
| ABES | Automated bonding evaluation system |
| CLP | Colloidal Lignin Particles |
| DL | Dirty Lignoboost |
| EtOH | Ethanol |
| PDADMAC | Polydiallyldimethylammonium chloride |
| PF | Phenol-formaldehyde |
| TEMPO | 2,2,6,6-Tetramethylpiperidine-1-oxyl |
| THF | Tetrahydrofuran |
| TONFC | Tempo oxidized nanofibrillar cellulose |
| UF | Urea-Formaldehyde |

# 1 Introduction

Replacing environmentally toxic materials with greener and naturally safe solutions has gained increasing interest among scientists. One area of interest has been the possibility to replace part of the toxic compounds in wood adhesives with more environmentally friendly solutions.

The replacement of, as an example, phenol in wood adhesives has been observed since phenol is a petroleum based chemical, it is expensive and toxic. The substitute which has been researched recently is lignin. As a non-toxic and inexpensive compound, lignin is a potential replacement for phenol in wood adhesives. Studies have shown that in particleboards phenolated lignin give better mechanical and physical properties than untreated lignin when they are used to substitute a part of the phenol in phenol-formaldehyde adhesives. In addition, phenolated lignosulfonate modified foaming resole adhesive has physical and mechanical properties equivalent to phenol-formaldehyde (PF) foams of fossil origin. (Goodman & Dodiuk, 2013, p. 612-614)

However, the lignin has been studied to be a poor binder in wood-based composites. Studies have shown that lignin itself is not adequate adhesive for wood-based composites but replacing some of the phenol in PF glues with lignin does not decrease the adhesive strength properties significantly. (Goodman & Dodiuk, 2013, p. 613; Hemmilä et al., 2013, p. 98-99)

The objective of this master's thesis was to test how colloidal lignin particles could be used in wood adhesives both in dry conditions. In addition, for some adhesives also the wet strength was observed. This objective was achieved by producing adhesives with PDADMAC coated colloidal lignin particles mixed with either tempo oxidized nano fibrillar cellulose or uncoated CLP and testing the glue joint strengths of these adhesives with Automated Bonding Evaluation System (ABES). In addition, a short trial was made in which the Dirty Lignoboost

lignin (*Valmet, Finland*) was mixed with PF in varying solid content ratios. These adhesives were then tested with ABES to study the glue joint strength.

The thesis is divided into two sections consisting of literature review and experimental part. The purpose of the literature part is to give some background information of, as an example, lignin and wood adhesives. The experimental section consists of methodology, results and discussion.

## 2 Lignin

Lignum is a latin word meaning wood, the word lignin derives from this word. Lignin can be found in many natural, or bio-based, resources. Different types of wood are not the only resources of lignin and thus lignin can be found also in vascular plants, such as grass and club mosses. Lignin is a common bio-based polymer since, as an example, wood contains significant amounts of it; approximately 20% in hardwoods and between 15-35% in softwoods. The amount of lignin in vascular plants vary between 1-20%. (Ek et al., 2009, p. 121, 124)

Lignin can be found from all plants that grow on land. In addition, lignin can be found in some plants growing underwater. Lignin has been studied over 100 years, but the scientists have not yet found any common structure and debate continues regarding it. It has been observed that the structure varies depending on the origin of the lignin. However, there have been some key characteristics studied that exist in lignin. These characteristics include following: lignin is plant-based polymer and contain majority of the methoxyl located in wood. In addition, lignin is made from phenylpropanoid units (Sun, 2010, p. 169)
From natural resources, lignin is the second most common polymer. The purpose of lignin in various plants is to act as a binder. (Goodman & Dodiuk, 2013, p. 612-613) Lignin has been studied to be a poor binder in wood composites with no other binders in them, but by replacing portion of phenol in phenol-formaldehyde glues with lignin the adhesion properties of the glues were unchanged. The formaldehyde emissions were also decreased, thus improving the environmental friendliness of the glue. (Goodman & Dodiuk, 2013, p. 613)

Lignin has an important role in woody plants. Without lignin, the cell walls of woody plants would not be as stiff as they are. Lignin has also an important role in binding the various cells together. In other words, lignin has an impact both

inside and outside the cell walls. Lignin has also strong water repelling characteristics and thus it makes the cell walls hydrophobic. (Ek et al., 2009, p. 124-125)

Lignin is a polymeric compound which together with cellulose and hemicellulose construct the wood cells. Lignin can be considered as the binding agent that binds together the cellulose fibers. This is the reason why wood can be considered as a composite in which cellulose fibers give the strength and lignin is the glue. The structure of lignin is overly complex, lignin can be considered as the bio-based polymer which has the most complicated structure in it. Lignin has both aromatic and aliphatic groups. Lignin is not a linear or branched polymer like cellulose and hemicellulose, but instead a polymer with a three-dimensional structure. In this structure the monomers are connected to ether and carbon-carbon – bonds. Ether bonds are C-O-C – bonds so they have carbon and oxygen atoms. The monomers which can be found in lignin are called p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The amount of each of these monomers are depending on which type of lignin is observed. Small amounts of p-coumaryl alcohol, only traces of sinapyl alcohol and large amounts of coniferyl alcohol can be found in softwoods. In hardwoods there are approximately 1:1 – 1:3 – ratio of coniferyl and sinapyl alcohols. P-coumaryl alcohol can be found in some hardwoods and in small amounts. Grass lignin includes more p-coumaryl than other lignins. In addition, it includes all these three monomers. (Ek et al., 2009, p. 121-123) In lignin the carbon bonds or ether bonds have hydroxyl and phenolic groups. The phenol-propane units are linked together with these bonds. This makes lignin a three-dimensional polymer with aromatic characteristics. (Goodman & Dodiuk, 2013, p. 612)

Although lignin has been used to substitute a portion of phenol in phenol-formaldehyde glues without decreasing the adhesion properties, lignin and phenol do not have the same structure. Lignin tends to react poorly with formaldehyde compared to the reaction between formaldehyde and phenol.

This can be explained with the fact that phenol has as many as five sites available for reaction, including para and ortho sites. In lignin, there are less sites available with para and ortho sites mostly reserved. In total, mostly more than one out of two sites are blocked in lignin. This decreases the cross-linking reactivity between lignin and formaldehyde. There is a possibility to increase the reactivity of lignin by, as an example, phenolation and sulfur-mediated demethylation. In Phenolation, lignin is mixed with phenol which has been treated with organic solvents. Mostly with ethanol or methanol. This mixture is heated and condensed, thus improving the reactivity. In demethylolation the methyl groups in aromatic rings are removed. (Goodman & Dodiuk, 2013, p. 613-614) From figure 1 can be seen the color of lignin dissolved in water, tetrahydrofuran (THF) and ethanol.

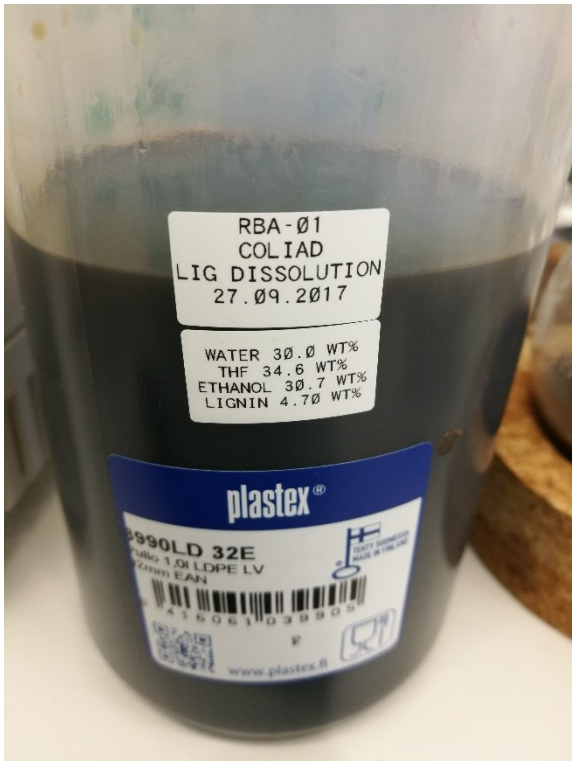


*Figure 1: Lignin dissolution in plastic bottle.*

## 3 Colloidal lignin particles (CLPs)

Kraft lignin is a side product of biorefinery industries, such as pulping industry. The common way to utilize the kraft lignin is to generate energy from it. Lignin has been found to have potential to be used more efficiently. The global regulations and agreements have increased the research around lignin. The possibility to enhance lignin in such manor that it could be used in various material application has been studied significantly. One possible option for this type of enhancement is to produce CLPs of kraft lignin. (Leskinen et al, 2017, p. 586-587)

Colloidal lignin particles (CLPs) are refined particles of kraft lignin. CLPs can be manufactured with various methods, such as nanoprecipitation process. In this process the lignin is in an organic solvent and the CLPs are created by adding a non-solvent in the mixture. Water is commonly used as the non-solvent. (Leskinen et al, 2017, p. 586-587)

The CLPs have many good properties compared to regular lignin. Colloidal lignin particles are round and have negative surface charge. These properties are important factors that make the CLPs more stable in water-based solutions compared to regular lignin. In addition, colloidal lignin particles possess, as an example, different surface chemistry properties compared to kraft lignin which make CLPs more usable as a raw material. (Leskinen et al, 2017, p. 586-587) Figure 2 shows the color of CLP solution.

## 4 Tempo oxidized nano fibrillar cellulose (TONFC)

TEMPO oxidization is a commonly used method to modify the cellulose fibers prior to mechanical treatment to convert the polysaccharide C6 primary hydroxyl groups to charged carboxyl units (Haniffa et al, 2017, p. 92). In TEMPO oxidization some of the hydroxyl groups of cellulose fibers are introduced with carboxylic groups (Salminen, 2017, p. 16). These carboxylic groups are ionized which causes repulsive forces between the nanofibrils of the cellulose fibres. This reaction causes the nanofibrils to separate more easily (Haniffa et al, 2017, p. 92). TEMPO method needs salts, such as natrium bromide (NaBr) and natrium chloride (NaCl), to work properly. In addition, the PH value has an important role. TEMPO/NaBr/NaClO – system has been used widely with PH value approximately 10. (Salminen, 2017, p. 16; Haniffa et al, 2017, p. 92).

Studies have shown that TEMPO oxidization doesn't affect the structure of the cellulose fibers nor cellulose nano crystals significantly, thus enabling the method to be used in modification of cellulose nano crystals (Salminen, 2017, p. 16; Haniffa et al, 2017, p. 92).

Figure 3 shows the mixing process of TONFC into water. The TONFC gel is dissolved into water for easier application in further stages.


*Figure 2: CLP solution in a glass flask.*

*Figure 3: TONFC dissolved into water under continuous stirring.*

## 5 Wood adhesion

The final quality of the adhesion in plywood is not only the result of the resin quality. Numerous factors that influence the adhesion exists. The resin itself is naturally a key factor, but also the wood itself play an important role in the adhesion. The factors can be divided into various groups. These groups include adhesive composition, wood property, wood preparation, adhesive application, wood geometry and product service factors. (Rohumaa, 2016, p. 18)

Adhesive composition factors are linked to the adhesive itself. These factors include mechanical factors such as strength and durability, molecular factors such as particle size, and the compound factors such as used solvents, fillers and catalysts. In addition, viscosity and rheology are part of the composition factors. Wood property factors include whole range of factors concerning the structure of wood and the changes the wood undergoes as it, as an example, interacts with the ambient air and is affected by surrounding forces. Wood property factors include for example species, strength, stability, sapwood, heartwood, springwood, summerwood, extractives, cellulose, lignin, decay and creep. Wood preparation factors concern, as an example, cutting to size, surface, moisture, impregnates and supply. Storage, weighing, mixing, application, ambient, pressure, temperature and press time are examples of adhesive application factors. Wood geometry factors include number of plies, ply organization, structure and architecture. Stress, external forces, creep, relaxation and environmental factors are examples of product service factors. (Rohumaa, 2016, p. 18)

Extractives have a significant impact on the wood-bonding properties. Acidic extractives can affect the curing in acid cured resins by decreasing curing time and increase the curing time in alkaline cured resins. Water-soluble extractives can have significantly negative impact on the bonding properties of cement

bonded wood boards. Water repelling extractives can prevent proper adhesion between wood surface and adhesive. (Roffael, 2016, p. 89-93)

Adhesion can be described as a phenomenon related to many different fields of science. Studies have shown that it is difficult to explain how the adhesion mechanisms exactly work. This is a result of the fact that adhesion is influenced by many factors, such as rheology, macromolecular science, and micromechanics. It is possible that multiple factors affect the adhesion and bonding at the same time. Adhesion theories include mechanical interlocking and weak boundary layer. (Rohumaa, 2016, p. 19)

Mechanical interlocking theory is based on the hypothesis that the adhesive penetrates the surface. The adhesive penetrates the pores and cavities thus bonding the materials together. The weak boundary layer can be used for determination of the magnitude of adhesion. The weak boundary layer can be a result of adhesive, adherent or environment factors or a mixture of these. The adhesive and adherent based weak boundary layer occur if impurities of the surface form a bond with the resin. Studies have shown that the bonding is positively affected by surface roughening. The more porous the surface is, the stronger the bonds are. However, too rough surfaces, as an example in wood, may cause weaker bonds. (Rohumaa, 2016, p. 19)

### 5.1 Phenol formaldehyde resins

Formaldehyde based resins have been used for decades. The use of formaldehyde in adhesives is significant in wood-based products, such as plywood and wood-based composites. Formaldehyde based adhesives cover more than 50% of the total volume of all adhesives used annually. They are easy to produce and require low investments to start producing. Urea-formaldehyde (UF) and phenol-formaldehyde (PF) adhesives are a couple of formaldehyde-based resins. In addition, they are thermosetting which means

that they harden in right temperature and this transformation cannot be reversed. (Goodman & Dodiuk, 2013, p. 13)

Phenol-formaldehyde (PF) glue was developed during the first decade of 20th century. It is one of the first commercial synthetic polymer-based adhesives. PF glues can be manufactured with a process called step-growth polymerization. In this process phenol is mixed with formaldehyde with the help of a catalyst, which is usually acidic. The phenol-formaldehyde adhesives usually include phenol, formaldehyde and hexamethylene tetramine as major ingredients. The ortho and para sites of phenol tend to react with the formaldehydes hydroxyl group thus making it possible for formaldehyde to join the aromatic ring of phenol. During this process methylene bridges are developed between the aromatic rings. (Goodman & Dodiuk, 2013, p. 14-16, 611)

Fractional distillation of coal tar and other synthetic processes are usually conducted to harvest phenol. These synthetic processes include, as an example, Dow and Cumene processes. Cumene process has been used for almost seven decades. In cumene process benzene and propylene are mixed together with aluminum chloride catalyst. This process develops isopropyl benzene which is also known as cumene. Cumene is broken down to phenol and acetone with the help of dioxygen and acid. In Dow process chloro benzene and sodium hydroxide are reacted with each other in temperature of 300℃ and pressure of 4000 psi. (Goodman & Dodiuk, 2013, p. 15)

The catalytic oxidation, or dehydrogenation, of methanol generates formaldehyde. In this reaction a copper oxide catalyst is heated to temperature varying between 300-600℃. Eventually, a mixture of methanol vapour and air is sprayed above the catalyst. Water and formaldehyde are generated during the process. Hexamethylene tetramine is produced at room temperature through reaction between ammonia gas and 30%(w:w) formaldehyde. (Goodman & Dodiuk, 2013, p. 15-16)

The phenol-formaldehyde ratio explains the depth of the cross-linking between these substituents. In an ideal situation the ratio is one. In this occasion all the phenols can be cross-linked through methylene bridges. The phenol-formaldehyde glues can be divided to two categories: Novolacs and Resoles. In Novolacs the phenol-formaldehyde ratio is less than one and an acidic catalyst is used. The Novolac polymerization itself can be triggered by acids, which is the first stage. The reaction proceeds relatively slow. To cross-link the resins a second stage is needed in which a hardener is added to the system. Resoles are phenol-formaldehyde glues which have the ratio above one and alkaline catalyst is used. The formaldehyde-phenol-ratio is usually between 1.1-1.5. The polymerization process is a single step process without an addition of hardeners. The reactions in single step processes occur between 70-120℃. During the process, first, the various groups are formed and the actual cross-linking occur when the process temperature is risen to 120℃. In resoles, the curing is needed for hardening and stability and they are called as one-step phenolics. The name derives from the fact that resoles need only one step, heat, to cure. The main products in which the resole type glues are used include plywood and oriented strand board (OSB). However, resoles tend to have a shelf-life from less than 2 months to 1 year, whereas novolacs preserve forever. (Goodman & Dodiuk, 2013, p. 16, 19-20, 613-614)

Phenolic adhesives in common have dark, opaque, color and this tend to limit their use. In addition, they can be manufactured to various forms, including liquid and powder forms. They are usually quite brittle which lead to the use of various fillers such as wood flour and cellulose to improve the adhesive and the desired characteristics. Phenolic adhesives can be used, as an example, in bonding, molding and laminating purposes. (Goodman & Dodiuk, 2013, p. 20-21, 23)

### 5.2 Lignin based adhesives

The use of lignin in wood adhesives has been of wide interest. (El Mansouri et al., 2007, p. 65; Ferdosian et al., 2017, p. 1) This is mostly due to the fact that lignin is a significant side product in pulp industries. In addition, the non-toxic nature of lignin is of key interest since the possibility to produce environmentally friendly adhesives has gained interest. (El Mansouri et al., 2007, p. 65-66) The use of lignin in adhesives has been studied, as an example, by replacing parts of either phenol-formaldehyde or urea-formaldehyde resins with it. Lignin itself has been studied to react poorly with formaldehyde, but this problem has been overcome by manufacturing methylolated lignin and mixing it with formaldehyde. Combination of methylolated lignin and phenol-formaldehyde adhesive has been used, as an example, in plywood manufacturing. (El Mansouri et al., 2007, p. 65)

Lignin is a polyphenol and thus it is thought to act the same way as phenol. (Ang et al., 2019, p. 2; Ferdosian et al., 2017, p. 2) However, lignin has lower reactivity than phenol. This can be explained by the fact that lignin, compared to regular phenol, has fewer free sites, such as para and ortho sites, in its aromatic nuclei. Due to lignin's poor reactivity, the lignin-based adhesives usually require further modification to produce adhesives. These modifications include adding more acid catalysts and longer heating times.

The use of lignin as the only resin ingredient has been studied widely. The studies indicate that longer heating times and higher temperatures in pressing are required to achieve sufficient bonding. Possible lignin modifications include also phenolation and hydrolysis. (Ang et al., 2019, p. 2-3) Studies have shown that kraft lignin can be used to substitute as much as 50-wt% of phenol in plywood adhesives, the pressing time must be increased though to gain sufficient bonding. Studies have shown that it is possible to gain better bonding strengths by replacing 50-wt% of phenol with eucalyptus bark lignin. Also, soda lignin can be used to substitute up to 50% of phenol in PF resins to gain

increased bonding strengths compared to regular PF resins. By replacing as much as 30% of phenol with organosolv lignin, has been reported to give internal bonding strengths comparable to regular phenol resins in particle board manufacturing. (Ang et al., 2019, p. 7-8)

Lignin has been used also in numerous environmentally friendly adhesives. These adhesives include lignin-tannin based adhesives and lignin-furfural based adhesives. Lignin-tannin adhesives have been used in wood panels designed for interior use. The adhesive consisted of 94% of environmentally friendly ingredients. Particleboards and plywood fulfilled standards when lignin-tannin adhesive was used. (Ang et al., 2019, p. 8) The combination of furfural and lignin produce environmentally friendly adhesive which has been reported to be suitable for fiberboard manufacturing. (Ang et al., 2019, p. 9)

# 6 Materials and methods

## 6.1 Materials

The used wood material consisted of birch veneer with thickness of 1.2mm from Southern Finland. The used chemical compounds consisted of 2-wt% tempo oxidized nano fibrillar cellulose KL001, 1.7-wt% tempo oxidized nano fibrillar cellulose, 4.7-wt% lignin stock RBA001, 100-wt% spray dried CLPs, 20-wt% Polydiallyldimethylammonium chloride (PDADMAC)(*Sigma Aldrich, Germany*), PF140J25 phenol-formaldehyde stock (*Prefere Resins Oy, Finland*), 5.64-wt% CLP stock KL945 and Dirty Lignoboost (*Valmet, Finland*). All adhesives and substances that were manufactured during this thesis had a unique code starting with letters NT and following with three numbers, such as NT002. The constituents of these adhesives and substances are explained in chapters 6 and 7 of this thesis and also in appendixes.

## 6.2 Methods

An important part of the experimental work was to manufacture various stock dispersions of cationic lignin particles, anionic coated lignin particles and anionic tempo oxidized nano fibrillar cellulose. Stock dispersions were eventually used to create adhesives through electrostatic forces. Stock dispersions consisted of, as an example, cationic (i.e., positively charged ions) or anionic (i.e., negatively charged ions) molecules.

Intrinsically anionic stock dispersions of colloidal lignin particles (CLPs, NT002 & NT015) were prepared by adding lignin dissolved in THF, EtOH and water into water in glass flask under continuous stirring. The CLPs formed immediately after impact because of mixing of the organic lignin solution with water. The colloidal particles are formed instantly as one substance is mixed into another substance. The less aggregates and sedimentation, the more stable the colloidal dispersion is. The CLPs were used in further experiments. CLP stock

dispersion (NT042) was prepared by adding spray dried CLPs (100-wt%) into a glass flask containing water.

Polydiallyldimethylammonium chloride (PDADMAC) is a cationic polyelectrolyte. Cationic CLPs were coated with PDADMAC to change the negatively charged surface to positive charge. Stock dispersions of PDADMAC coated colloidal lignin particles (CLP: PDADMAC, NT003 & NT016) were prepared by adding lignin dissolved in THF, EtOH and water into a glass flask containing PDADMAC (20-wt%). PDADMAC was added 3-wt% of the CLPs solid content. The pouring was made slowly in both dispersions and under continuous stirring. The stock solutions were further processed, and part of the organic solvents were removed by rotary evaporation at 40 °C under vacuum to reach solid contents of 1.67-wt%(NT003) and 1.71-wt%(NT016).

Stock dispersions of water diluted tempo oxidized nano fibrillar cellulose (TONFC, NT005, NT018, NT029 & NT054) were prepared by adding TONFC (1.7 or 2.0-wt%) into water. Dispersions were made into glass flasks and TONFC was added in one go under continuous stirring. Stirring was continued approximately an hour until the compounds were visually mixed together. Figure 4 shows the experimental setup from single constituents to adhesives and further.

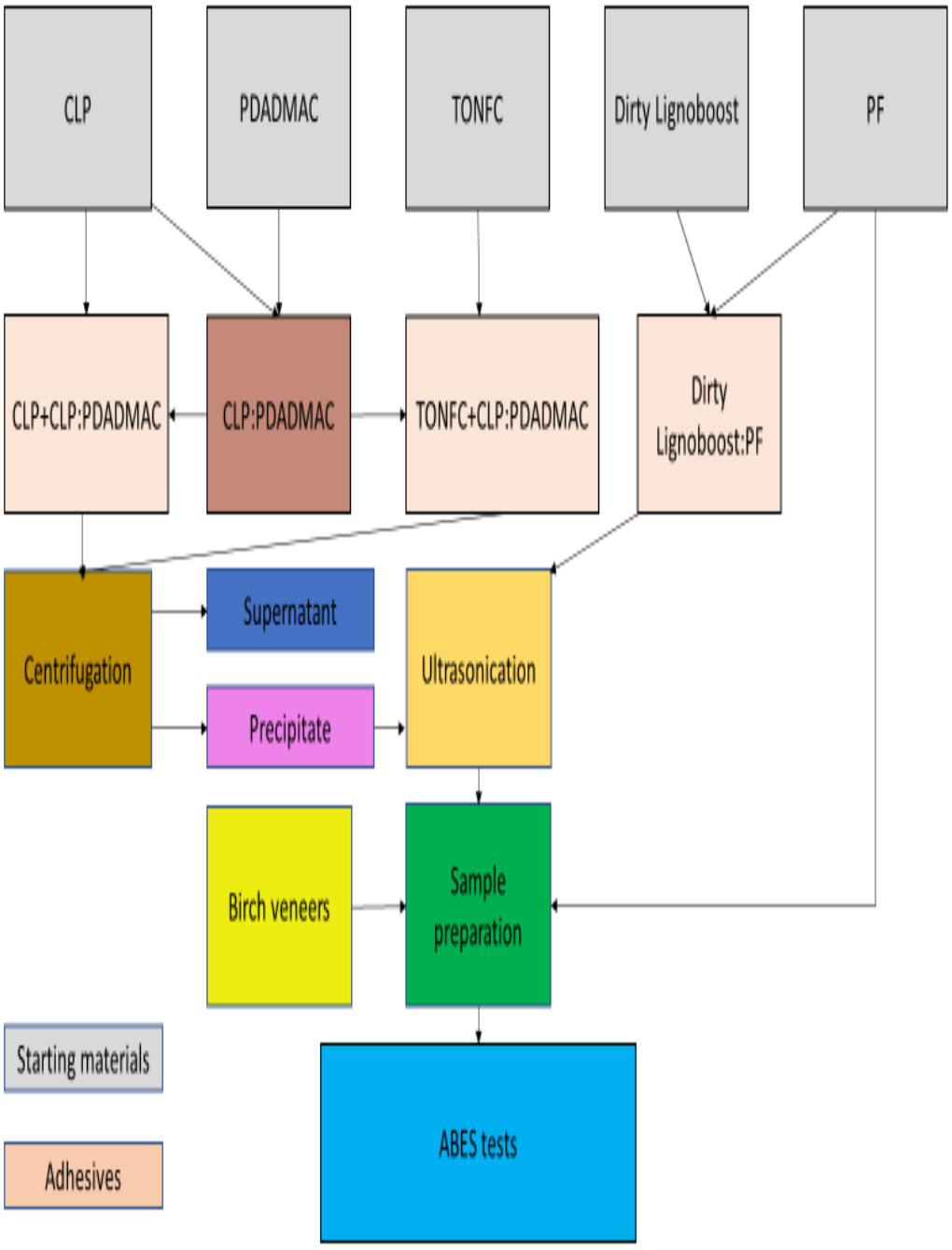


*Figure 4: The path of adhesive manufacturing.*

### 6.2.1 Electrostatic aggregates of positively charged CLPs and negatively charged TONFCs

Electrostatic aggregation was used to form adhesives. Aggregation occurred as positively charged CLPs were mixed with negatively charged TONFCs. This formula was tested to see whether TONFC can improve adhesion properties of CLP adhesives. This method was used with dispersions NT013, NT019- NT026, NT030-NT041 and NT056. The adhesives were prepared by pouring water diluted TONFC into a glass flask containing PDADMAC coated CLPs. Solutions were weighed so that the TONFC/ (TONFC+CLP: PDADMAC) solid content ratio was 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, 50.0, 60.0, 80.0 or 90.0%. The pour was made slowly, and the mixture was under continuous stir. The aggregated dispersions were ultrasonicated for approximately 5 minutes to ensure proper mixing of the CLPs and TONFCs. Dispersions NT013, NT019-NT026, NT030-NT041 and NT056 were then filtered under vacuum to separate supernatant and precipitate. Precipitate was then gathered and ultrasonicated for approximately 5 minutes for proper mixing. After ultrasonication the precipitate was ready to be used in ABES tests. Figure 5 shows the mixture of TONFC and CLP, and figure 6 shows the different end products after the solution in figure 5 has been filtered.

*Figure 5: Mixture of TONFC and CLP.*

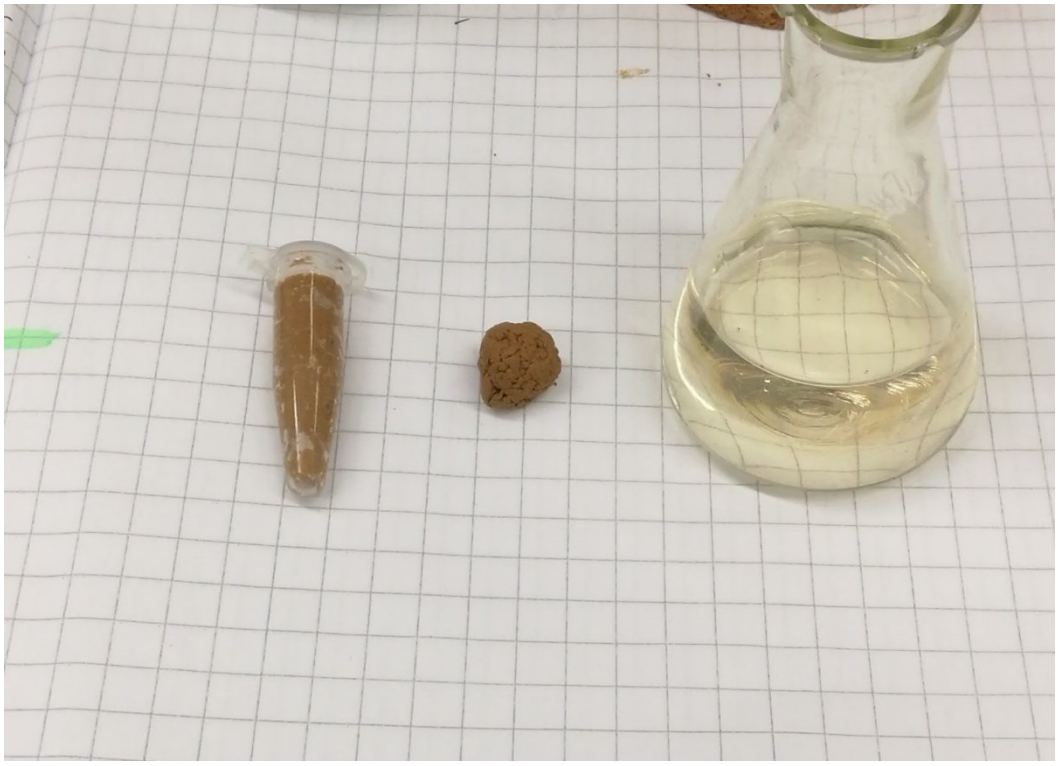

*Figure 6: Brown precipitate and clear supernatant.*

### 6.2.2 Electrostatic aggregates of positively and negatively charged CLPs

Electrostatic aggregation was used to form adhesives. CLPs with positive and negative surface charge was aggregated to see how CLP-CLP adhesive performs as a wood binder. This method was used with dispersions NT043, NT048-NT052, NT055 and NT057-NT058. The adhesives were prepared by pouring intrinsically negative CLPs into a glass flask containing PDADMAC coated CLPs. PDADMAC coating was done to change the electrostatic charge of the CLPs from negative to positive. Solutions were weighed so that the CLP: PDADMAC/ (CLP+CLP: PDADMAC) solid content ratio was 10.0, 20.0, 30.0, 40.0, 50.0, 60.0 or 70.0%. The pour was made slowly, and the mixture was under continuous stir. Negatively charged CLPs were added into the CLP: PDADMAC approximately one tenth at a time. Partial additions were made to ensure that the negatively charged CLPs were coated with positively charged CLPs properly. The electrostatically aggregated dispersions were then centrifugated to separate supernatant and precipitate. Precipitate was then gathered to be used in ABES tests. Figure 7 shows solution ready to be centrifugated.

*Figure 7: Solution in centrifuge tube.*

### 6.2.3 Formulation of colloidal lignin particles with phenol-formaldehyde resin

Dirty Lignoboost lignin (DL) and phenol-formaldehyde (PF) resin were weighed into a 2.0 ml Eppendorf test tube so that the PF/(PF+DL) mass ratio was approximately 20.0, 30.0, 40.0, 60.0 or 80.0%. The dispersions were then ultrasonicated for 5 minutes for proper mixing of the PF and DL. The dispersions were stored for two days in a refrigerator and then used in ABES tests. The viscosity of these adhesives weren't measured.

### 6.2.4 Automated bonding evaluation system

Automated bonding evaluation system (ABES) is an instrument which can be used to measure the tensile strength of the adhesive joint between two pieces of, as an example, wood veneer. The size of the adhesive joint is approximately 5mm x 20mm and the common volume of the adhesive droplet is 8.6 microliters. The measuring parameters that can be changed include temperature, pressing time and compression. The glue joint is compressed between two heated plates for desired duration and then the test pieces are pulled in opposite directions to measure the tensile strength of the joint. The tensile strength can be measured instantly after the compression or later. ABES results can be used as a guideline for predicting how the adhesives would work in, as an example, plywood. Figure 8 shows test pieces made with ABES machine and figure 9 shows the ABES machine.

ABES (Adhesive Evaluation Systems, Incorporated) was used in these studies to gain information how strong the glue joints are with different glues and in dry and moist samples. In addition, the effect of the pressing temperature on the tensile strength was studied. Pressing time was set to 160 seconds, the pressing temperature was set between 90℃ - 190℃ and the compression was 2 bar. The volume of the used glue in test pieces was between 8.6-43.0 microliters. The adhesive was applied with spoon or electronic micropipette (HandyStep electronic, Brand GmbH+CO, Germany) Every glue was tested 1-5 times and the

average of the tensile strength results was calculated. The glue joint tensile strength was tested for both dry and, in some cases, soaked samples. For soaking tests, the dry samples were compressed between the hot plates, then soaked in water for 24 hours. After that, the glue joint tensile strength was tested. The ABES tests were divided into sections such as: the effect of the TONFC/(TONFC+CLP:PDADMAC) and CLP:PDADMAC/(CLP+CLP:PDADMAC) solid content ratio on the glue joint tensile strength, PF/(PF+DL) mass ratio on the glue joint tensile strength, the effect of pressing temperature and the droplet volume on the glue joint tensile strength.

*Figure 8: Test pieces ready for testing.*

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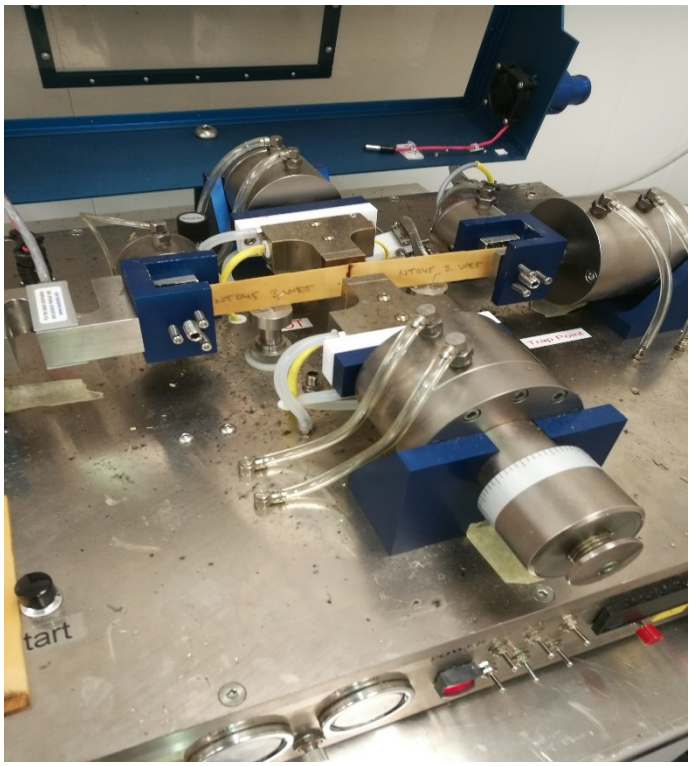

*Figure 9: ABES machine.*

# 7 Results

The first set of adhesives consisted of samples NT004, NT007, NT008, NT009, NT011-NT014. These adhesives were electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with the TONFC/ (TONFC+CLP: PDADMAC) solid content ratios of 5%, 10%, 15%, 20%, 30%, 40% and 90%. Visually the samples were uniform and had the same color and structure. The dosage for ABES tests was approximately 20 microliters and the adhesive was added with a small spoon. Adhesive was added with a spoon due to its thick consistency. Each adhesive was tested 1-5 times. The highest shear strength results were achieved with samples NT004 and NT013, which both had the solid content ratio of 20%. The worst result was achieved with sample NT008, which had the solid content ratio of 5%. From figure 10 can be seen that the values peak at around 20% solid content ratio and under and above this point they eventually decrease. The addition was made with a spoon which made it difficult to estimate the exact amount of adhesive applied and there is a significant chance for large variations. Automated tip head was used in further studies to ensure as consistent dosages as possible.

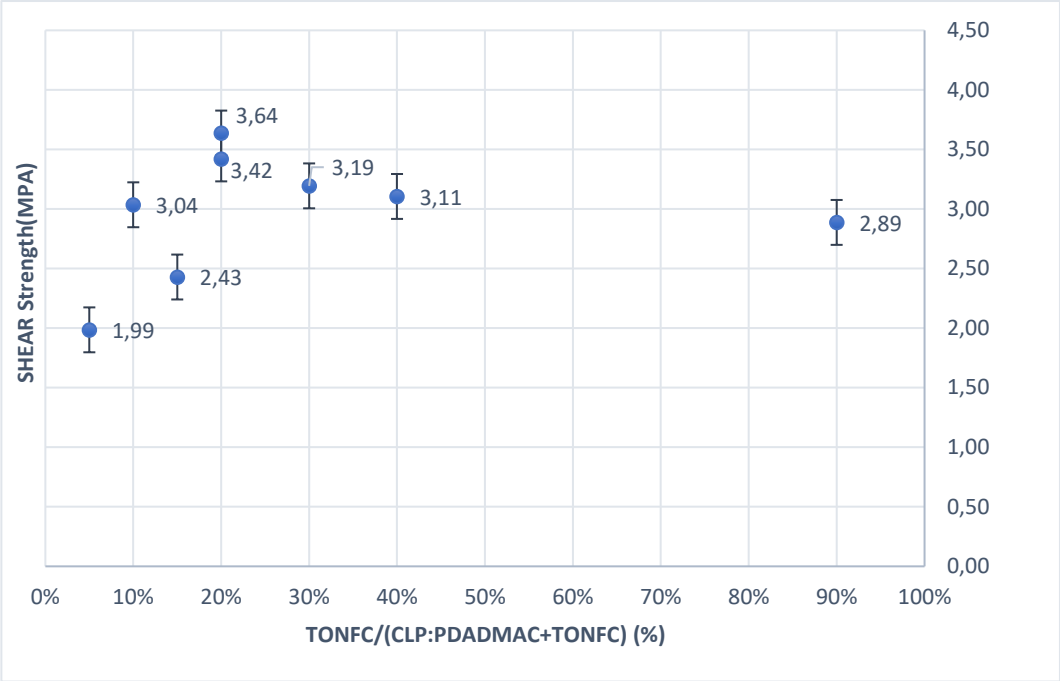


*Figure 10: ABES results of electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with dosage of approximately 20 microliters.*

Since the highest values were gotten with the solid content ratio of 20%, this ratio was kept as the ideal ratio and it was studied more extensively. The next set of adhesives consisted of samples NT019-NT024. The dosage was set to 8.6 microliters and the adhesive was applied with automated pipette. The adhesives were electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with the TONFC/ (TONFC+CLP: PDADMAC) solid content ratios of 2.5%, 15%, 20%, 25%, 60% and 80%. Highest values were achieved with solid content ratios of 15% and 20%. The values were less than of those achieved with approximately 20 microliters dosage with equal solid content ratio. In addition, all samples had poorer glue joint shear strength properties than the reference glue which was a gel with TONFC solid content of 1.7%. With closer inspection, while using the regular unmodified tip head, it could be seen that the adhesive inside the tip included a lot of moisture. It is possible that the CLP: PDADMAC + TONFC aggregates were too big in size for the regular tip head and therefore could not pass the tip head and the results were poorer since the added adhesive was mostly fluid. Figure 11 shows the results.

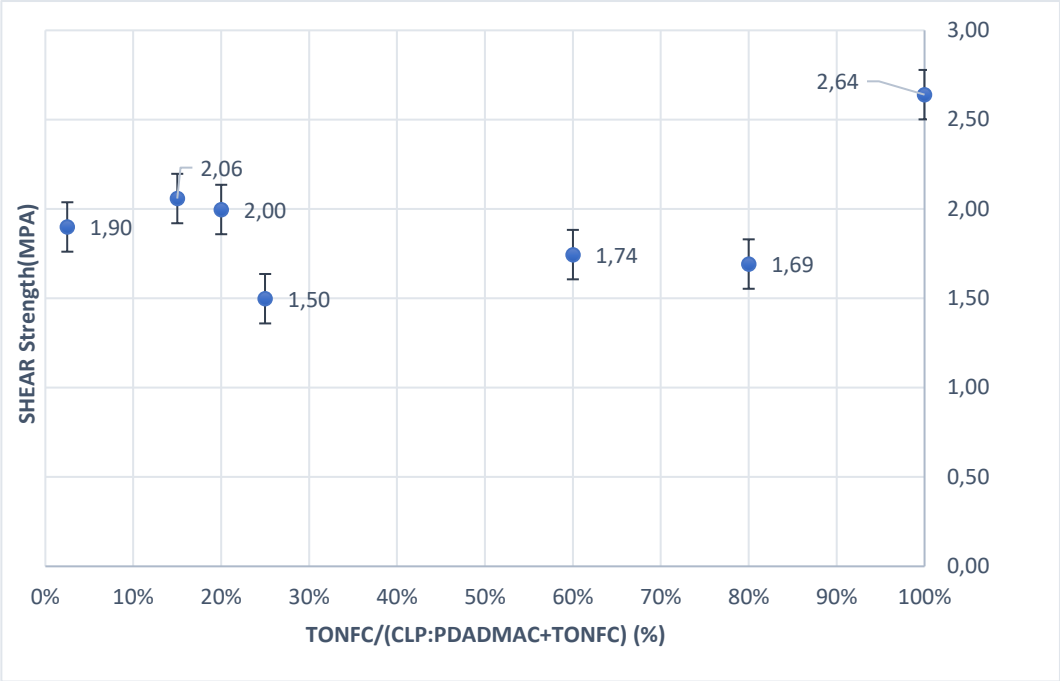


*Figure 11: ABES results of electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with 8.6 microliter dosage.*

The same glues were used for another set of ABES tests excluding the 100% TONFC solid content ratio reference (TONFC solids content of 1.7%) and 2.5% solid content ratio glue. The difference for the previous set was that the tip head was cut so that the diameter of the tip head expanded significantly. The modification was done with the hypothesis that wider tip head allows more solids to enter the pipet and thus improve the ABES results. It can be seen from figure 12 that the tip head modification had a significant impact on the ABES tests. The average shear strengths increased in every sample and the glues with 15% and 20% solid content ratios had the best strength properties. The shear strength results of the first set of samples were significantly higher, as an example, in the 20% solid content ratio glue. Thus, a hypothesis was made that the increase in the total mass of solids increase the shear strength. The hypothesis was tested in further studies by testing how different dosages affect the shear strength values of the glue joints.

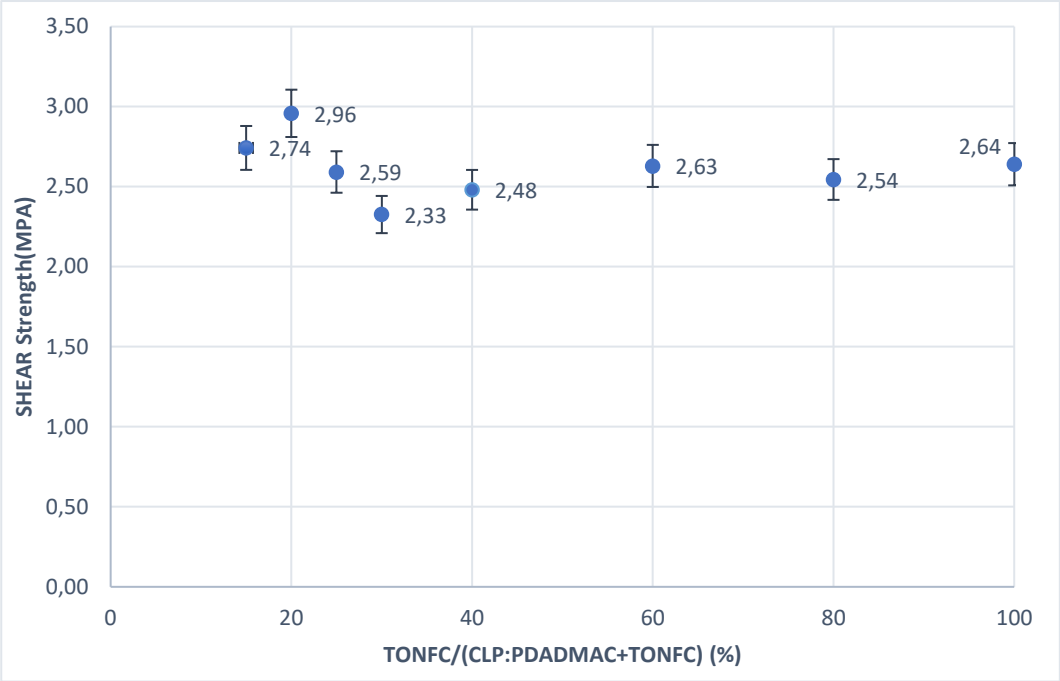


*Figure 12: ABES results of electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with 8.6 microliter dosage and modified tip head.*

The glue with 20% TONFC/ (TONFC+CLP: PDADMAC) solid content ratio had the best shear strength so it was tested more extensively. The previously mentioned hypothesis was tested with the 20% TONFC/ (TONFC+CLP: PDADMAC) solid content ratio glue (NT023) and the dosages were 8.6, 17.2, 25.8, 34.4 and 43.0 microliters. As can be seen from figure 13, the dosage had an impact on the shear strength of the glue joint. The best shear strength was achieved with 34.4 microliter dosage. The strength difference between the best two dosages (17.2 and 34.4 microliters) was less than 1%, however. In addition, it seems that increasing the dosage may not increase the shear strength of the glue joint. One possible reason for the zigzagging results is that the glue inside the pipet may have had very uneven number of solids and therefore the results do not have any linearity.

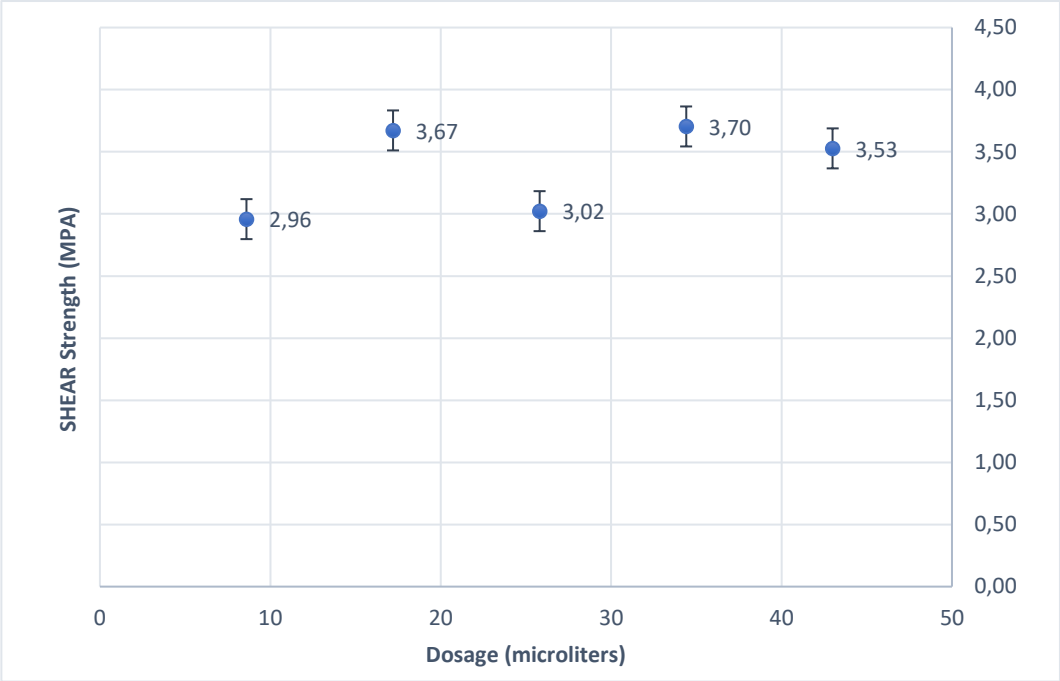


*Figure 13: ABES results of electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with 8.6–43.0 microliter dosage and modified tip head.*

As the ideal TONFC/ (TONFC+CLP: PDADMAC) solid content ratio and dosage had been figured out, the next step was to observe how the pressing temperature affected the shear strength of the glue joints. In total, 9 different pressing temperatures were tested. These temperatures were 90, 92.5, 95, 100, 110, 130, 150, 170 and 190℃. The used glue was NT023 which had TONFC/ (TONFC+CLP: PDADMAC) solid content ratio of 20%. The idea was to observe the smallest temperature in which the glue joint can be formed between the veneers and observe higher pressing temperatures. The test trial started with pressing temperature of 130℃. After this temperature was tested, the pressing temperature was decreased 10℃ at a time until the critical point was reached. The idea was to decrease the temperature until glue joints did not form between the veneers. The critical point was approximately 90℃. The next part of the tests was to observe how strong glue joints can be achieved with temperatures above 130℃. The average shear strengths are presented in table 1.

*Table 1: Average shear strengths with various pressing temperatures.*

| Sample | Information, dosage, temp. | Average shear strength(MPa) |
|---|---|---|
| NT023 | Modified tip, 34.4microL, 90℃ | 0,15 |
| NT023 | Modified tip, 34.4microL, 92.5℃ | 0,91 |
| NT023 | Modified tip, 34.4microL, 95℃ | 1,47 |
| NT023 | Modified tip, 34.4microL, 100℃ | 2,15 |
| NT023 | Modified tip, 34.4microL, 110℃ | 3,37 |
| NT023 | Modified tip, 34.4microL, 130℃ | 3,70 |
| NT023 | Modified tip, 34.4microL, 150℃ | 3,86 |
| NT023 | Modified tip, 34.4microL, 170℃ | 4,55 |
| NT023 | Modified tip, 34.4microL, 190℃ | 4,71 |

From figure 14 can be seen that the shear strength increased as the pressing temperature increased. At 90℃, the adhesive failed to form a bond between the veneers. In addition, figure 15 indicates that the most significant increase in the shear strength occurred between temperatures ranging from 90℃ to 110℃. When pressing temperatures are observed in temperature intervals of 90-110℃ and 110-190℃ the shear strength increased quite linearly in both intervals. This can be seen in figures 15 and 16. The glue NT023 was also tested in wet tests with the following test parameters: dosage of 34.4 microliters and pressing temperature of 130℃. The adhesive failed to form a firm bond between the veneers, however.

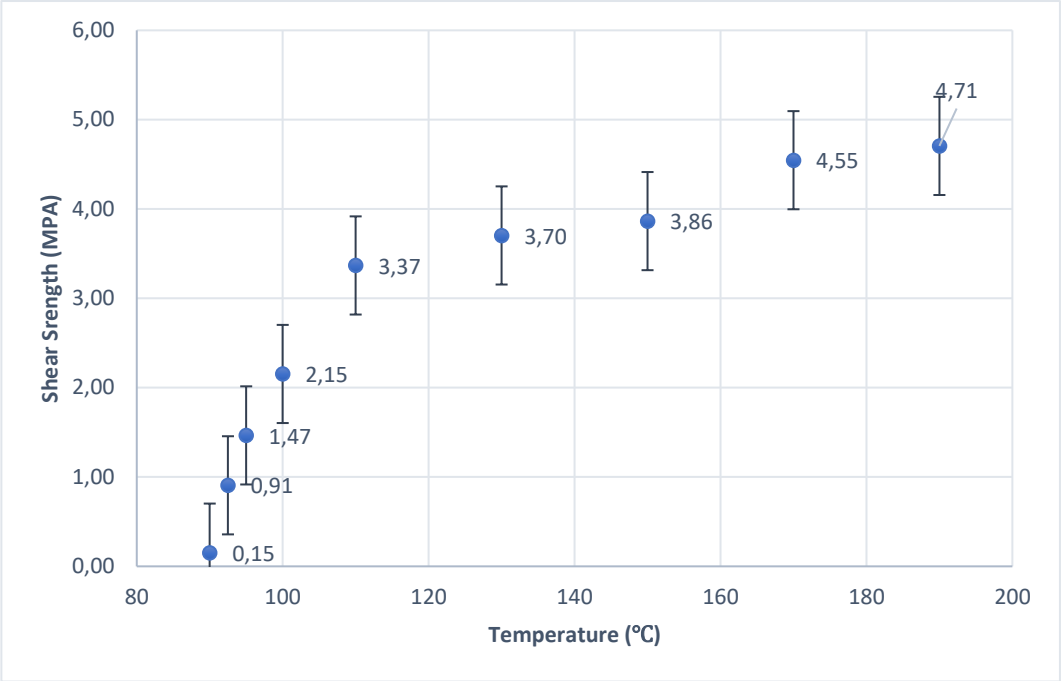


*Figure 14: Effect of pressing temperature (90-190 ℃) on shear strength.*

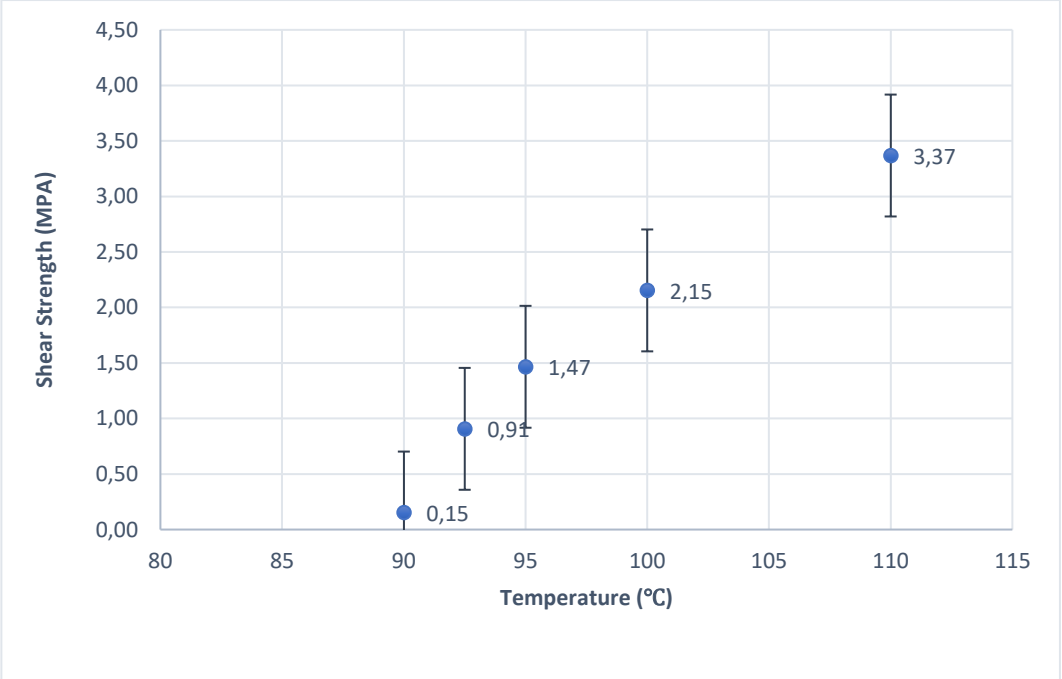


*Figure 15: Effect of pressing temperature on shear strength between 90–110 ℃.*

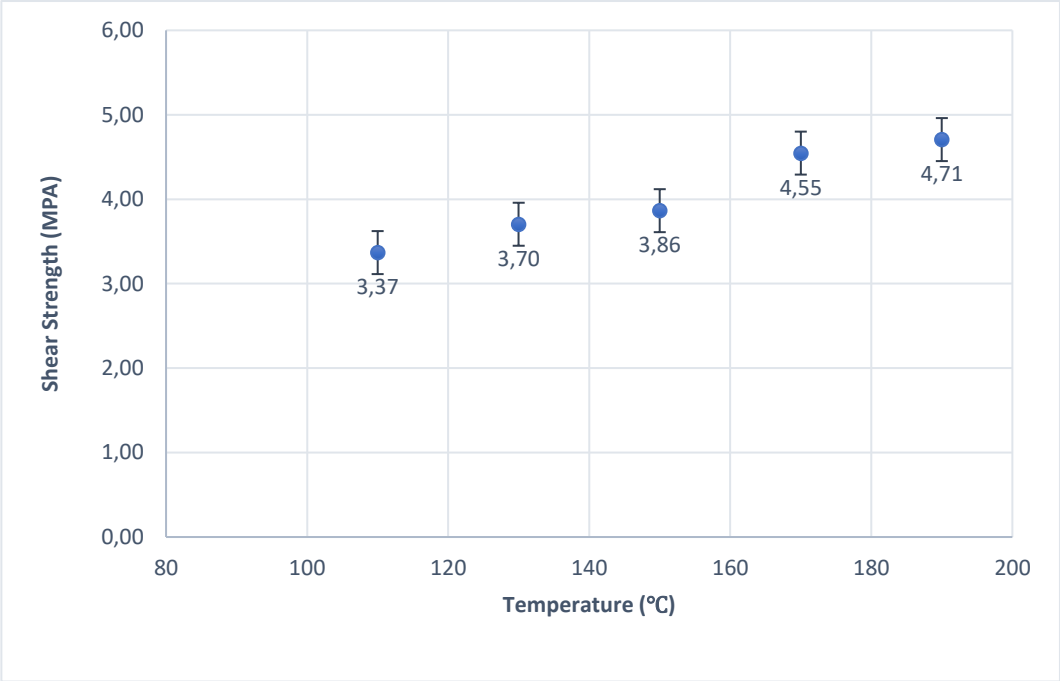


*Figure 16: Effect of pressing temperature on shear strength between 110–190℃.*

The final set of glues including TONFC had the TONFC/(TONFC+CLP:PDADMAC) solid content ratios of 2.5, 5, 10, 15, 20, 25, 30, 40, 60, 80, 90, 100% with codes NT030-NT040 and REF2. The set also included a 20% solid content ratio glue (NT041) which had been washed with 250ml of water to separate salt from the glue. The pressing temperature was 130℃ and the dosage was 34.4 microliters. The shear strength tests indicate that the highest shear strength averages were achieved with glue that had solid content ratio of 25%. In addition, it seems that the water washed glue with 20% solid content ratio was stronger than the unwashed glue with the same ratio. The water washed glue formed second strongest bonds. The results indicate that glues with ratios of 2.5%-15% and shear strength averages between 2.58MPa-2.77MPa were close to the reference glue with average shear strength of 2.66MPa. The results can be seen from figure 17. The water washing had a significant impact on the glue joint strength, and therefore it should be studied more extensively, as an example, by conducting a test trial with full set of glues and with the same TONFC/(TONFC+CLP:PDADMAC) solid content ratios. In addition, the moisture durability of the water washed glues should be also tested.

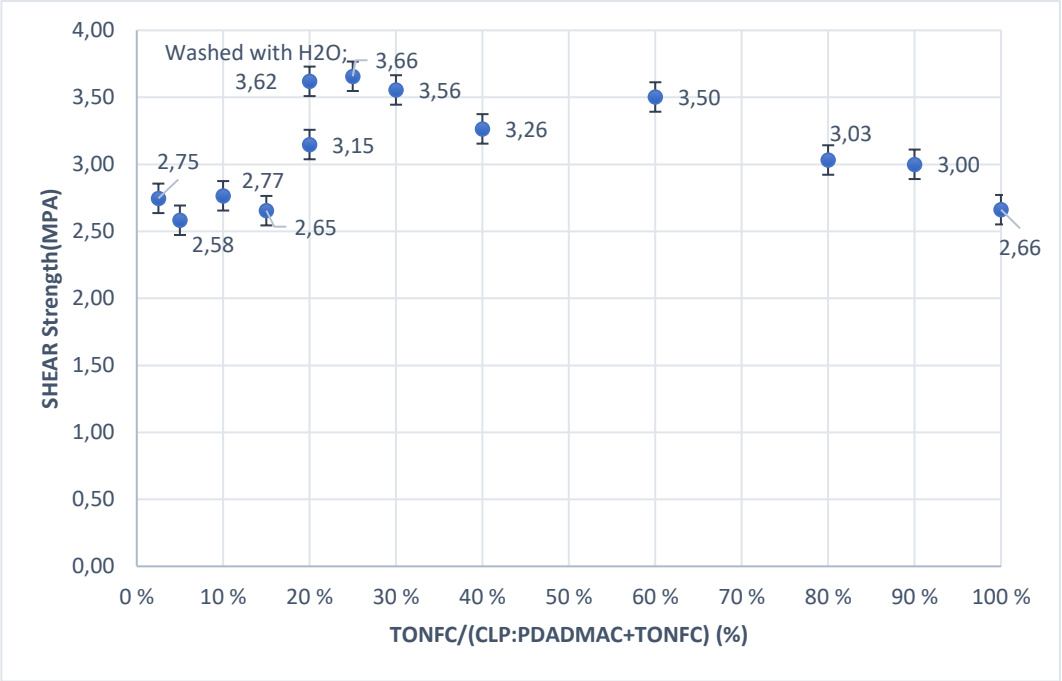


*Figure 17: ABES results of reference glue, and electrostatic aggregates of positively charged CLPs and negatively charged TONFCs with 34.4 microliter dosage and modified tip head.*

Combination of Dirty Lignoboost and Phenol formaldehyde was tested to observe how the addition of Dirty Lignoboost affects the glue joint shear strength properties both in dry and water-soaked samples. Five different PF/ (PF + Dirty Lignoboost) volume ratios were tested. These ratios were 20%, 30%, 40%, 60% and 80%. Plain Phenol formaldehyde was also tested to gain reference values. The dry sample shear strength test results indicate that the glue joints shear strength increased as the proportion of phenol formaldehyde was increased, and the highest shear strength values were gained with plain phenol formaldehyde. Water soaked samples had poorer glue joint shear strength values as expected. However, it can be seen from figure 18 that the 60% and 80% phenol formaldehyde proportions led to higher glue joint shear strength values compared to plain phenol formaldehyde. This indicates that substituting 20% and 40% of phenol formaldehyde with Dirty Lignoboost leads to improvement in wet conditions.

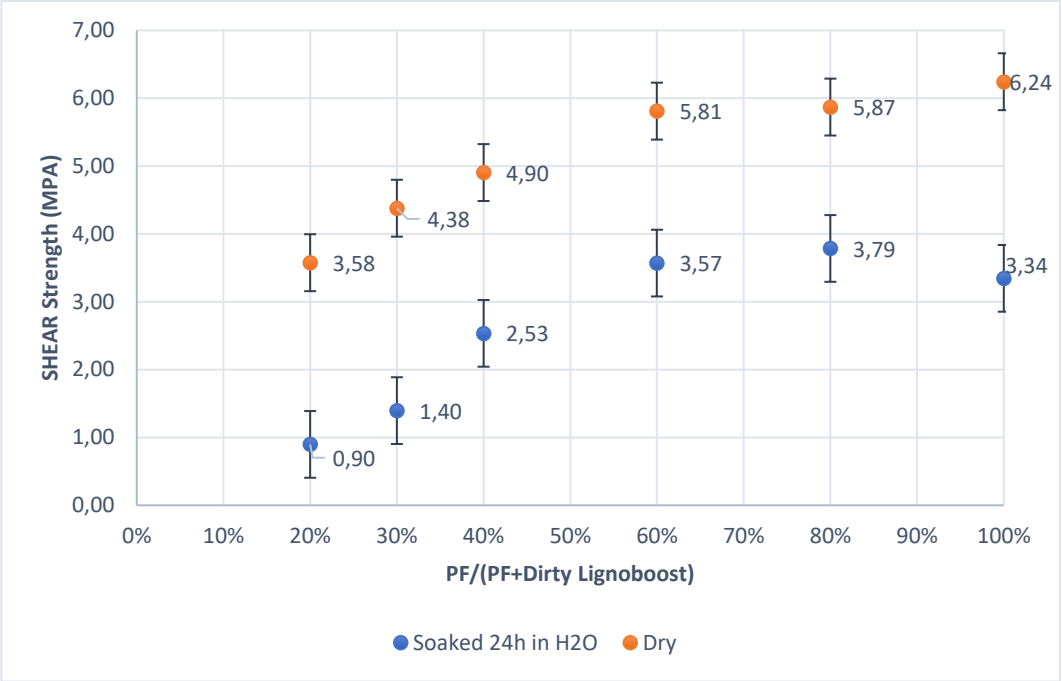


*Figure 18: Wet and dry sample ABES results of plain phenol formaldehyde, and combination of dirty lignoboost and phenol formaldehyde with 8.6 microliter dosage and unmodified tip head.*

The final set of glues were a combination of PDADMAC coated CLPs mixed with CLPs. The dosage was 8.6 microliters and the tip head was unmodified. The tested CLP: PDADMAC/ (CLP: PDADMAC+CLP) ratios were 10%, 20%, 30%, 40%, 50%, 60% and 70%. The worst shear strength was 3.27MPa and it was achieved with 50% ratio. The highest value was 3.69MPa and it was gained with 40% ratio. The difference between the highest and smallest value was approximately 0.42MPa, which is relatively small difference. In addition, it seemed that there was not a correlation in the increase of CLP: PDADMAC/ (CLP: PDADMAC+CLP) ratio. However, the results indicate that the worst CLP: PDADMAC/ (CLP: PDADMAC+CLP) ratio produces stronger glue joints than many of the glue joints made of TONFC + CLP: PDADMAC. This can be seen by comparing figures 10, 11, 12, 13, 17, 18 and 19. Further studies should be made to determine how CLP + CLP: PDADMAC glues withstand moisture.

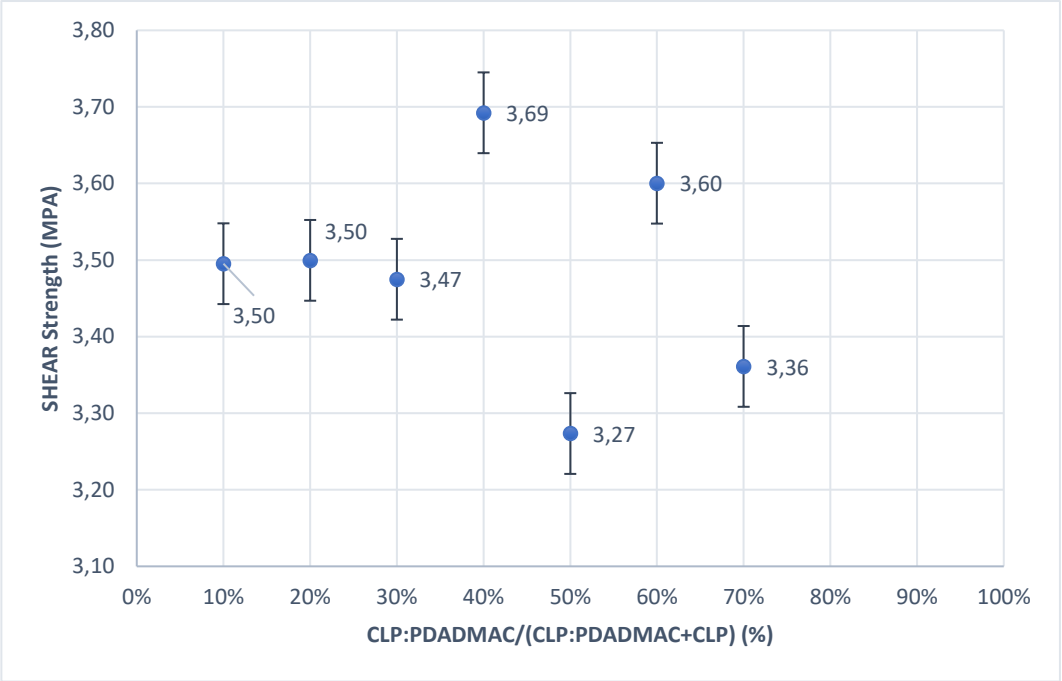


*Figure 19: ABES results of CLPs mixed with PDADMAC coated CLPs, 8.6 microliter dosage and unmodified tip head.*

Regular phenol-formaldehyde resin was tested with 8,6 microliters dosage and unmodified tip head with ABES to gain reference value. The average dry shear strength was 6.24MPa. Results show that all shear strength values of manufactured CLP-based adhesives in dry samples were significantly smaller than values gained with 100-wt% PF resin. According to Rohumaa et al. (2014) the average shear strength of PF in ABES tests can be as high as 6.14MPa depending on the plywood manufacturing parameters. The studied average of 6.23MPa is close to this.

## 8 Discussion

The comparison to other studies is difficult since the used wood species and pressing parameters can vary significantly. In addition, the use of adhesives made of CLPs is quite novel which makes it hard to find results gained with similar adhesive compositions. Studies made with other bio-based adhesives can be found and the results gained in this thesis have been compared with them.

Esteves et al. (2019) studied how pressing time effects the shear strength of adhesive joint between two beech wood (*Fagus sylvatica*) veneers. Adhesive was made either of the liquefied bark or branches of southern blue gum tree (*Eucalyptus globulus*). In addition, the adhesives were tested in temperatures of 100°C and 130°C with pressing time between 0 to above 300 seconds. According to the results gained by Esteves et al. these bio-based adhesives had shear strength values between 0-1.70 MPa for bark adhesive and 0-1.94 MPa for branch adhesive. The highest values were achieved with pressing times exceeding 300 seconds. The values gained with temperature of 130°C and pressing time of 150 seconds are approximately 0.9 MPa for bark adhesive and 1.4 MPa for branch adhesive. While comparing these values to the ones gained in the experimental part of this thesis it can be seen that all of the adhesives gained higher shear strength results compared to the values gained by Esteves et al. while using the same pressing temperature of 130°C and pressing time of 160 seconds, which is close to the pressing time of 150 seconds used by Esteves et al. The smallest value gained in this thesis was approximately 1.69 MPa which is over 10% higher compared to the highest value gained by Esteves et al. Both the study made by Esteves et al. and this thesis indicate that the increase of pressing temperature increases the shear strength.

Lorenz et al. (2015) studied the shear strength of soy adhesives with pressing time of 120 seconds and pressing temperature of 120°C. The

results show that soy-based adhesives gain shear strength of at least 4.6 MPa. This is significantly higher than the results gained in this thesis. Only the samples with PF:Dirty Lignoboost ratio of above 40% had higher shear strength compared to the minimum value gained by Lorenz et al.

Ghorbani et al. (2016) studied adhesives combined of PF, and lignin of various sources. They had used pressing times varying between 30-720 seconds with pressing temperature of 120°C. Their study shows that samples made of adhesive with PF:Lignin ratio of 60% or 80% and pressing time of 120 seconds gained shear strength varying approximately between 2-3.5 MPa. The results gained by Ghorbani et al. indicate that as the proportion of lignin increases, the shear strength of the samples decrease. This same conclusion can be made with the data collected in this thesis. The adhesives with PF:Dirty Lignoboost ratios of 60% and 80% gained shear strength values between 5.81-5.87 MPa which is significantly higher than values gained by Ghorbani et al. However, this difference could be explained by the 10°C lower pressing temperature and 40 seconds lower pressing time used by Ghorbani et al.

According to Rohumaa et al. (2014) the average shear strength of PF in ABES tests can be as high as 6.14MPa depending on the plywood manufacturing parameters. The studied average of 6.23 MPa is close to this. The pressing parameters used by Rohumaa et al. were close to the ones used in this thesis with pressing time of 120 seconds and pressing temperature of 130°C. Ghorbani et al. had the same pressing time and 10°C lower pressing temperature compared to Rohumaa et al. but gained significantly lower PF reference value (~3.5 MPa). This difference between the PF reference value gained in this thesis, Rohumaa et al. study and Ghorbani et al. study could be explained, as an example, by the different wood species used in veneers.

# 9 Conclusions

The objective of this thesis was to test how colloidal lignin particles could be used in wood adhesives in dry conditions. In addition, some adhesives were tested also for their wet strength. Three types of adhesives were made. The adhesives including colloidal lignin particles were made by using the electrostatic aggregation of oppositely charged particles. The adhesive types were the following: positively charged CLPs were mixed with negatively charged TONFCs to form adhesive, negatively charged CLPs were mixed with positively charged CLPs to form adhesive and Dirty Lignoboost lignin was mixed with PF to form adhesive.

The results indicate that the adhesives including colloidal lignin particles do not possess as high glue joint strength as the PF glue. In addition, the wet strength of the CLP adhesives was poor and mostly the glue joints failed before the actual ABES test had even begun. This indicates that the CLP based adhesives cannot form waterproof bonds. This should be investigated further to see if the bonding in moist conditions could be enhanced. The tests in dry conditions showed that CLP based adhesives can form bonds, but not as strong as regular PF adhesive. The results were promising, but further studies should be made to see if the bonding strength could be improved. One possible option for further studies could be to see how removing of salts from the CLP adhesive effect the bonding strength. This was studied very shortly during the experimental part of the thesis for the sample NT034 which was washed with 250ml of water. The results showed that the washing improved the bonding strength approximately 15% compared to unwashed sample of the same adhesive.

In overall, there was not any correlation between bonding strength of the various solid content ratios in CLP samples. The ideal solid content ratio of adhesives including tempo oxidized nano fibrillar cellulose and CLP seemed to be between 20-30% (TONFC/(TONFC:CLP)). This uneven correlation may be

caused by the errors during the manufacturing of the adhesives and during the application of the adhesive during the ABES tests. The “mouth” of the micro pipette, which as used for the application, was small and it seemed like it was flocked very often so that moisture came out excessively instead of the actual binding compounds. These tests should be repeated so that the application of the adhesives would be as even as possible to improve even application of the adhesives.

The electrostatically formed adhesives of positive and negative colloidal lignin particles showed higher bonding strengths in general compared to the adhesives formed of CLP and TONFC. The variation of bonding strength between different solid content ratios was also smaller. This may indicate that the CLP-CLP adhesives did not flock the pipette and spread more evenly on the test samples in ABES tests. These tests could be repeated so that the effect of washing the samples would be studied and to see if moisture could be removed from the adhesives more efficiently.

The final part of the experimental section was to test how adding dirty lignoboost lignin to the PF adhesive affects the bonding strength. The dry condition results showed that compared to regular PF adhesive, the more dirty lignoboost lignin was added the weaker was the bonding strength. However, the wet tests showed that the bonding strength of adhesives that had dirty lignoboost lignin 20% and 40% of total solid contents had better bonding strength compared to regular PF. This should be studied further to see what causes these results. These results were promising since the bonding strength of the dry samples including adhesives containing dirty lignoboost lignin 20% and 40% of total solid contents was 6-7% weaker but the wet samples, containing these two adhesives, had 7-13% higher bonding strength compared to regular PF adhesive.

In overall, all tests should be repeated in such manner that the effects of possible errors during the experimental part could be reduced. The possible

errors were caused by mistakes in calculations, during the laboratory tests and in general through human errors. Good ways to improve the reliability of the tests would be to improve the application of the adhesives during the ABES tests by using proper instruments and using more reliable ways to reduce the moisture content from the adhesives.

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**APPENDIX 1.** Average ABES tests results.

| | | Measurements (N) | | | | | |
|---|---|---|---|---|---|---|---|
| Sample(TONFC%) | 1 | 2 | 3 | 4 | 5 | Notes + dosage | Average(MPa) |
| NT004(20%) | 378,14 | 359,89 | 353,32 | | | Added with spoon ~20microL | 3,637833333 |
| NT007(10%) | 303,56 | | | | | Added with spoon ~20microL | 3,0356 |
| NT008(5%) | 198,56 | | | | | Added with spoon ~20microL | 1,9856 |
| NT009(40%) | 286,1 | 390,5 | 264,4 | 348,2 | 263,5 | Added with spoon ~20microL | 3,1054 |
| NT011(15%) | 235,7 | 248,2 | 266,4 | 221,3 | | Added with spoon ~20microL | 2,429 |
| NT012(30%) | 274,4 | 351,8 | 332,1 | | | Added with spoon ~20microL | 3,194333333 |
| NT013(20%) | 429,9 | 254,7 | 402,9 | 312,4 | 310,4 | Added with spoon ~20microL | 3,4206 |
| NT014(90%) | 268 | 299,3 | 327,8 | 259,9 | | Added with spoon ~20microL | 2,8875 |
| NT019(2,5%) | 252,58 | 212,43 | 160,6 | 169,36 | 154,76 | Small tip head 8,6microL | 1,89946 |
| NT020(60%) | 167,91 | 183,96 | 135,05 | 219 | 166,44 | Small tip head 8,6microL | 1,74472 |
| NT020(60%) | 263,53 | 247,47 | 299,3 | 201,48 | 302,95 | Big tip head 8,6microL | 2,62946 |
| NT021(80%) | 127,02 | 183,23 | 192,72 | 185,42 | 157,58 | Small tip head 8,6microL | 1,69194 |
| NT021(80%) | 229,2 | 232,14 | 262,8 | 262,07 | 286,16 | Big tip head 8,6microL | 2,54474 |
| NT022(15%) | 175,2 | 200,02 | 191,26 | 229,22 | 233,6 | Small tip head 8,6microL | 2,0586 |
| NT022(15%) | 293,46 | 329,96 | 225,57 | 275,21 | 246,74 | Big tip head 8,6microL | 2,74188 |
| NT023(20%) | 181,77 | 194,91 | 202,94 | 186,88 | 232,14 | Small tip head 8,6microL | 1,99728 |
| NT023(20%) | 305,87 | 429,97 | 276,67 | 227,03 | 239,44 | Big tip head 8,6microL | 2,95796 |
| NT023(20%) | 448,22 | 332,15 | 386,17 | 351,86 | 317,55 | Big tip head 17,2microL | 3,6719 |
| NT023(20%) | 295,65 | 306,6 | 297,11 | 381,06 | 230,68 | Big tip head 25,8microL | 3,0222 |
| NT023(20%) | 302,22 | 471,58 | 362,81 | 317,55 | 397,85 | Big tip head 34,4microL | 3,70402 |
| REF 1. | 292,7 | 265,72 | 233,6 | | | 1,7% TONFC GEL 8,6microL | 2,640066667 |
| NT024(25%) | 164,98 | 121,18 | 133,59 | 154,03 | 175,2 | Small tip head 8,6microL | 1,49796 |
| NT024(25%) | 208,78 | 192,72 | 277,4 | 303,68 | 313,17 | Big tip head 8,6microL | 2,5915 |
| NT025(30%) | 216,81 | 273,02 | 181,77 | 223,38 | 267,91 | Big tip head 8,6microL | 2,32578 |
| NT026(40%) | 163,52 | 262,8 | 217,54 | 256,23 | 340,18 | Big tip head 8,6microL | 2,48054 |
| NT023(20%) | 360,62 | 357,7 | 362,81 | 316,82 | 365,73 | Big tip head 43microL | 3,52736 |
| NT023(20%) | 13,87 | 16,79 | | | | Big tip head 34,4microL 90°C | 0,1533 |
| NT023(20%) | 141,62 | 112,42 | 101,47 | 7,3 | | Big tip head 34,4microL 92,5°C | 0,907025 |
| NT023(20%) | 166,41 | 168,63 | 239,44 | 112,42 | 45,99 | Big tip head 34,4microL 95°C | 1,46578 |
| NT023(20%) | 215,35 | 236,52 | 246,01 | 176,66 | 202,21 | Big tip head 34,4microL 100°C | 2,1535 |
| NT023(20%) | 329,96 | 370,84 | 274,48 | 373,03 | 335,8 | Big tip head 34,4microL 110°C | 3,36822 |
| NT023(20%) | 302,22 | 471,58 | 362,81 | 317,55 | 397,85 | Big tip head 34,4microL 130°C | 3,70402 |
| NT023(20%) | 356,24 | 365 | 395,66 | 424,13 | 391,28 | Big tip head 34,4microL 150°C | 3,86462 |
| NT023(20%) | 482,53 | 416,1 | 456,98 | 493,48 | 424,13 | Big tip head 34,4microL 170°C | 4,54644 |
| NT023(20%) | 386,17 | 465,74 | 560 | | | Big tip head 34,4microL 190°C | 4,706366667 |
| NT023(20%) | 18,25 | | | | | Big tip head 34,4microL, 130°C, wet test | 0,1825 |
| NT030(2,5%) | 311,71 | 266,45 | 242,36 | 245,28 | 307,33 | Big tip head 34,4microL 130°C | 2,74626 |
| NT031(5%) | 262,07 | 264,99 | 300,76 | 216,08 | 247,47 | Big tip head 34,4microL 130°C | 2,58274 |
| NT032(10%) | 223,38 | 321,93 | 251,12 | 308,79 | 277,4 | Big tip head 34,4microL 130°C | 2,76524 |
| NT033(15%) | 257,69 | 264,26 | 250,39 | 268,64 | 286,16 | Big tip head 34,4microL 130°C | 2,65428 |
| NT034(20%) | 346,02 | 331,42 | 311,71 | 325,58 | 259,15 | Big tip head 34,4microL 130°C | 3,14776 |
| NT041(20%) | 396,39 | 345,29 | 359,89 | 357,7 | 350,4 | Big tip head 34,4microL 130°C, washed with 250ml of H2O | 3,61934 |
| NT035(25%) | 372,3 | 332,88 | 395,66 | 342,37 | 385,44 | Big tip head 34,4microL 130°C | 3,6573 |
| NT036(30%) | 365 | 346,75 | 351,13 | 359,16 | 355,51 | Big tip head 34,4microL 130°C | 3,5551 |
| NT037(40%) | 291,27 | 357,7 | 270,1 | 367,19 | 346,02 | Big tip head 34,4microL 130°C | 3,26456 |
| NT038(60%) | 334,34 | 342,37 | 361,35 | 354,78 | 358,43 | Big tip head 34,4microL 130°C | 3,50254 |
| NT039(80%) | 305,87 | 286,16 | 329,23 | 309,52 | 285,43 | Big tip head 34,4microL 130°C | 3,03242 |
| NT040(90%) | 269,37 | 337,99 | 332,88 | 243,09 | 316,82 | Big tip head 34,4microL 130°C | 3,0003 |
| NT043(50:50) | 300,76 | 403,69 | 404,42 | 356,24 | 312,44 | Big tip head 34,4microL 130°C, CLP:PDAC-CLP dispersion | 3,5551 |
| REF 2. | 290,54 | 258,42 | 229,22 | 261,34 | 291,27 | 2,0% TONFC GEL 34,4microL | 2,66158 |
| NT044 | 317,55 | 356,97 | 353,32 | 341,64 | 418,29 | Small tip head 8,6microL, 80% Dirty Lignoboost + 20% PF | 3,57554 |
| NT045 | 462,82 | 564,29 | 532,91 | 420,48 | 471,58 | Small tip head 8,6microL, 60% Dirty Lignoboost + 40% PF | 4,90416 |
| NT046 | 562,1 | 473,77 | 671,6 | 650,43 | 546,77 | Small tip head 8,6microL, 40% Dirty Lignoboost + 60% PF | 5,80934 |
| NT047 | 583,27 | 602,98 | 645,32 | 559,91 | 543,12 | Small tip head 8,6microL, 20% Dirty Lignoboost + 80% PF | 5,8692 |
| NT044 | 123,37 | 102,93 | 64,97 | 81,03 | 76,65 | Small tip head 8,6microL, 80% Dirty Lignoboost + 20% PF, wet | 0,8979 |
| NT045 | 313,17 | 272,29 | 235,06 | 195,64 | 251,12 | Small tip head 8,6microL, 60% Dirty Lignoboost + 40% PF, wet | 2,53456 |
| NT046 | 296,38 | 288,35 | 522,68 | 308,06 | 369,38 | Small tip head 8,6microL, 40% Dirty Lignoboost + 60% PF, wet | 3,5697 |
| NT047 | 327,77 | 364,27 | 381 | 428,51 | 391,28 | Small tip head 8,6microL, 20% Dirty Lignoboost + 80% PF, wet | 3,78566 |
| NT048(50:50) | 317,55 | 337,26 | 315,36 | 318,28 | 348,28 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,27346 |
| NT049(70:30) | 322,66 | 318,28 | 296,48 | 398,58 | 344,56 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,36112 |
| NT050(30:70) | 405,15 | 319,01 | 343,1 | 307,33 | 362,88 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,47494 |
| NT051(60:40) | 316,82 | 346,02 | 356,97 | 356,24 | 424,13 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,60036 |
| NT052(40:60) | 354,05 | 348,21 | 388,36 | 365 | 390,55 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,69234 |
| NT057(20:80) | 326,31 | 359,16 | 380,33 | 361,35 | 322,66 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,49962 |
| NT058(10:90) | 356,24 | 287,62 | 354,78 | 370,11 | 378,87 | Small tip head 8,6microL 130°C, CLP:PDAC-CLP dispersion | 3,49524 |
| NT053 | 484,72 | 494,94 | 370,11 | 413,91 | 425,59 | Small tip head 8,6microL, 70% Dirty Lignoboost + 30% PF | 4,37854 |
| NT053 | 103,66 | 191,26 | 39,42 | 102,2 | 261,34 | Small tip head 8,6microL, 70% Dirty Lignoboost + 30% PF, wet | 1,39576 |
| PF140J25, ref. 3 | 610,28 | 586,19 | 685,47 | 705,91 | 533,63 | Small tip head 8,6microL, 100% PF | 6,24296 |
| PF140J25, ref. 3 | 321,2 | 308,06 | 298,57 | 349,67 | 394,93 | Small tip head 8,6microL, 100% PF, wet | 3,34486 |

**APPENDIX 2.** TONFC-water dispersions.

**NT005 concentration/TONFC-water dispersion**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| | Water | 152,32 | g |
| KL000 | TONFC 1,7% | 51,05 | g |
| | TONFC concentration | 1,70 % | |
| | diluted TONFC concentration | 0,43 % | % |

**NT018 concentration/TONFC-water dispersion**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| | Water | 180,63 | g |
| KL000 | TONFC 1,7% | 60,2 | g |
| | TONFC concentration | 1,7 | % |
| | diluted TONFC concentration | 0,424947 | % |

**NT029 concentration/TONFC-water dispersion**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| | Water | 133,63 | g |
| KL000 | TONFC 2% | 44,54 | g |
| | TONFC concentration | 2 | % |
| | diluted TONFC concentration | 0,499972 | % |

**NT054 concentration/TONFC-water dispersion**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| | Water | 128,41 | g |
| KL000 | TONFC 2% | 32,48 | g |
| | TONFC concentration | 2 | % |
| | diluted TONFC concentration | 0,403754 | % |

**APPENDIX 3.** CLP-water dispersions.

| NT002 concentration/CLP-water dispersion | | | |
|---|---|---|---|
| Code | Substance | Quantity | Unit |
| | Water | 86,96 | g |
| RBA-01 | lignin in THF:EtOH:water 4.67 % | 39,99 | g |
| | Concentration | 4,67 % | |
| | CLP concentration in mixture | 1,47 % | |

| NT015 concentration/CLP-water dispersion | | | |
|---|---|---|---|
| Code | Substance | Quantity | Unit |
| | Water | 438,48 | g |
| RBA-01 | lignin in THF:EtOH:water 4.67 % | 201,72 | g |
| | Concentration | 4,67 % | |
| | CLP concentration in mixture | 1,47 % | |

| NT042 concentration/CLP-water dispersion | | | |
|---|---|---|---|
| Code | Substance | Quantity | Unit |
| | Water | 491,5 | g |
| | spray dried CLP 100 % | 8,5 | g |
| | Concentration | 100,00 % | |
| | CLP concentration in mixture | 1,70 % | |

**APPENDIX 4.** CLP:PDADMAC mixture.

**NT003 concentration/CLP-PDAC mixture**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| NT002 | CLP Stock | 125,87 | g |
| RBA-01 | concentration | 1,47 % | % |
| | CLP dry mass | 1,851645 | g |
| | 20 wt. % PDAC stock | 0,37764 | g |
| | PDAC conc. | 20 % | |
| | PDAC dry mass | 0,075528 | g |
| | PDAC / CLP | 4,1 % | |
| | total solids | 1,53 % | |

**NT006 concentration/CLP-PDAC mixture-rotavaporated**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| NT003 | CLP-PDAC dispersion | 79,93 | g |
| | concentration | 1,53 % | |
| | solids | 1,220133 | g |
| NT006 | dispersion mass after rotavap | 72,91 | g |
| | concentration after rotavap | 1,67 % | |

| Concentration | Unit | Substance |
|---|---|---|
| 0,687952745 | % | CLP+PDAC |
| 0,022952666 | % | CLP+PDAC/rotavaporated |

**NT016 concentration/CLP-PDAC mixture**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| NT015 | CLP Stock | 640,2 | g |
| RBA-01 | concentration | 1,47 % | % |
| | CLP dry mass | 9,417839 | g |
| | 20 wt. % PDAC stock | 2,07 | g |
| | PDAC conc. | 20 % | |
| | PDAC dry mass | 0,414 | g |
| | PDAC / CLP | 4,4 % | |
| | total solids | 1,53 % | |

**NT017 concentration/CLP-PDAC mixture-rotavaporated**

| Code | Substance | Quantity | Unit |
|---|---|---|---|
| NT016 | CLP-PDAC dispersion | 635,26 | g |
| | concentration | 1,53 % | |
| | solids | 9,72453 | g |
| NT017 | dispersion mass after rotavap | 568,51 | g |
| | concentration after rotavap | 1,71 % | |

| Concentration | Unit | Substance |
|---|---|---|
| 0,687952745 | % | CLP+PDAC |
| 0,003008794 | % | CLP+PDAC/rotavaporated |

## **APPENDIX 5.** CLP:PDADMAC+TONFC mixtures.

| **NT013: 20% TONFC** | |
|---|---|
| 5,17 | g CLP:PDAC NT006 |
| 1,67 % | conc. CLP:PDAC NT006 |
| 0,086519 | g CLP:PDAC solids |
| 5,28 | g TONFC NT005 |
| 0,43 % | conc. TONFC NT005 |
| 0,022532 | g TONFC solids |
| 0,10905 | g total solids |
| 20,66 % | TONFC/(CLP:PDAC + TONFC) |

| **NT019: 2,5% TONFC** | |
|---|---|
| 25,36 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,433790224 | g CLP:PDAC solids |
| 2,56 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,010878645 | g TONFC solids |
| 0,444668869 | g total solids |
| 2,45 % | TONFC/(CLP:PDAC + TONFC) |

| **NT020: 60% TONFC** | |
|---|---|
| 5 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,085526 | g CLP:PDAC solids |
| 29,98 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,127399 | g TONFC solids |
| 0,212926 | g total solids |
| 59,83 % | TONFC/(CLP:PDAC + TONFC) |

| **NT021: 80% TONFC** | |
|---|---|
| 3 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,051316 | g CLP:PDAC solids |
| 48,02 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,20406 | g TONFC solids |
| 0,255375 | g total solids |
| 79,91 % | TONFC/(CLP:PDAC + TONFC) |

| **NT022: 15% TONFC** | |
|---|---|
| 10,22 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,174816092 | g CLP:PDAC solids |
| 7,21 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,030638683 | g TONFC solids |
| 0,205454775 | g total solids |
| 14,91 % | TONFC/(CLP:PDAC + TONFC) |

| **NT023: 20% TONFC** | |
|---|---|
| 11,4 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,195 | g CLP:PDAC solids |
| 11,45 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,048656 | g TONFC solids |
| 0,243657 | g total solids |
| 19,97 % | TONFC/(CLP:PDAC + TONFC) |

| **NT024: 25% TONFC** | |
|---|---|
| 9,04 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,154632 | g CLP:PDAC solids |
| 12,03 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,051121 | g TONFC solids |
| 0,205753 | g total solids |
| 24,85 % | TONFC/(CLP:PDAC + TONFC) |

| **NT025: 30% TONFC** | |
|---|---|
| 8,17 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,139750242 | g CLP:PDAC solids |
| 14,06 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,059747556 | g TONFC solids |
| 0,199497798 | g total solids |
| 29,95 % | TONFC/(CLP:PDAC + TONFC) |

| **NT026: 40% TONFC** | |
|---|---|
| 9,61 | g CLP:PDAC NT017 |
| 1,71 % | conc. CLP:PDAC NT017 |
| 0,164382 | g CLP:PDAC solids |
| 25,54 | g TONFC NT018 |
| 0,42 % | conc. TONFC NT018 |
| 0,108531 | g TONFC solids |
| 0,272913 | g total solids |
| 39,77 % | TONFC/(CLP:PDAC + TONFC) |

| **NT030: 2,5% TONFC** | |
|---|---|
| 41,96 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 2,366544 | g CLP:PDAC solids |
| 12,13 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,060647 | g TONFC solids |
| 2,427191 | g total solids |
| 2,50 % | TONFC/(CLP:PDAC + TONFC) |

| **NT031: 5% TONFC** | |
|---|---|
| 19,98 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 1,126872 | g CLP:PDAC solids |
| 11,87 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,059346669 | g TONFC solids |
| 1,186218669 | g total solids |
| 5,00 % | TONFC/(CLP:PDAC + TONFC) |

| **NT032: 10% TONFC** | |
|---|---|
| 10,21 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,575844 | g CLP:PDAC solids |
| 12,78 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,063896 | g TONFC solids |
| 0,63974 | g total solids |
| 9,99 % | TONFC/(CLP:PDAC + TONFC) |

| **NT033: 15% TONFC** | |
|---|---|
| 9,48 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,534672 | g CLP:PDAC solids |
| 18,89 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,094445 | g TONFC solids |
| 0,629117 | g total solids |
| 15,01 % | TONFC/(CLP:PDAC + TONFC) |

| **NT034: 20% TONFC** | |
|---|---|
| 5,48 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,309072 | g CLP:PDAC solids |
| 15,53 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,077645642 | g TONFC solids |
| 0,386717642 | g total solids |
| 20,08 % | TONFC/(CLP:PDAC + TONFC) |

| **NT035: 25% TONFC** | |
|---|---|
| 1,54 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,086856 | g CLP:PDAC solids |
| 5,82 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,029098 | g TONFC solids |
| 0,115954 | g total solids |
| 25,09 % | TONFC/(CLP:PDAC + TONFC) |

| **NT036: 30% TONFC** | |
|---|---|
| 1,77 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,099828 | g CLP:PDAC solids |
| 8,6 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,042998 | g TONFC solids |
| 0,142826 | g total solids |
| 30,10 % | TONFC/(CLP:PDAC + TONFC) |

| **NT037: 40% TONFC** | |
|---|---|
| 1,91 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,107724 | g CLP:PDAC solids |
| 14,48 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,072395936 | g TONFC solids |
| 0,180119936 | g total solids |
| 40,19 % | TONFC/(CLP:PDAC + TONFC) |

| **NT038: 60% TONFC** | |
|---|---|
| 0,62 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,034968 | g CLP:PDAC solids |
| 10,49 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,052447 | g TONFC solids |
| 0,087415 | g total solids |
| 60,00 % | TONFC/(CLP:PDAC + TONFC) |

| **NT039: 80% TONFC** | |
|---|---|
| 0,3 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,01692 | g CLP:PDAC solids |
| 13,51 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,067546 | g TONFC solids |
| 0,084466 | g total solids |
| 79,97 % | TONFC/(CLP:PDAC + TONFC) |

| **NT040: 90% TONFC** | |
|---|---|
| 0,23 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,012972 | g CLP:PDAC solids |
| 23,34 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,11669345 | g TONFC solids |
| 0,12966545 | g total solids |
| 90,00 % | TONFC/(CLP:PDAC + TONFC) |

| **NT041: 20% TONFC(washed with 250ml of H2O)** | |
|---|---|
| 5,44 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 0,306816 | g CLP:PDAC solids |
| 15,44 | g TONFC NT029 |
| 0,50 % | conc. TONFC NT029 |
| 0,077196 | g TONFC solids |
| 0,384012 | g total solids |
| 20,10 % | TONFC/(CLP:PDAC + TONFC) |

| **NT056: 20% TONFC** | |
|---|---|
| 41,42 | g CLP:PDAC KL945 |
| 5,64 % | conc. CLP:PDAC KL945 |
| 2,336088 | g CLP:PDAC solids |
| 144,59 | g TONFC NT029 |
| 0,40 % | conc. TONFC NT029 |
| 0,583788 | g TONFC solids |
| 2,919876 | g total solids |
| 19,99 % | TONFC/(CLP:PDAC + TONFC) |

**APPENDIX 6.** CLP:PDADMAC+CLP mixtures, and solid contents(%)

| NT043: 50% CLP:PDAC + 50% CLP | | |
|---|---|---|
| 30,01 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 1,692564 | g CLP:PDAC solids | |
| 99,56 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 1,69252 | g CLP solids | |
| 3,385084 | g total solids | |
| 50,00 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT048: 50% CLP:PDAC + 50% CLP | | |
|---|---|---|
| 10,34 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,583176 | g CLP:PDAC solids | |
| 34,3 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,5831 | g CLP solids | |
| 1,166276 | g total solids | |
| 50,00 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT049: 70% CLP:PDAC + 30% CLP | | |
|---|---|---|
| 9,96 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,561744 | g CLP:PDAC solids | |
| 14,13 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,24021 | g CLP solids | |
| 0,801954 | g total solids | |
| 70,05 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT050: 30% CLP:PDAC + 70% CLP | | |
|---|---|---|
| 4,67 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,263388 | g CLP:PDAC solids | |
| 36,16 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,61472 | g CLP solids | |
| 0,878108 | g total solids | |
| 29,99 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT051: 60% CLP:PDAC + 40% CLP | | |
|---|---|---|
| 8,12 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,457968 | g CLP:PDAC solids | |
| 17,97 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,30549 | g CLP solids | |
| 0,763458 | g total solids | |
| 59,99 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT052: 40% CLP:PDAC + 60% CLP | | |
|---|---|---|
| 8,82 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,497448 | g CLP:PDAC solids | |
| 43,89 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,74613 | g CLP solids | |
| 1,243578 | g total solids | |
| 40,00 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT057: 20% CLP:PDAC + 80% CLP | | |
|---|---|---|
| 3,34 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,188376 | g CLP:PDAC solids | |
| 44,31 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,75327 | g CLP solids | |
| 0,941646 | g total solids | |
| 80,00 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| NT058: 10% CLP:PDAC + 90% CLP | | |
|---|---|---|
| 1,74 | g CLP:PDAC KL945 | |
| 5,64 % | conc. CLP:PDAC KL945 | |
| 0,098136 | g CLP:PDAC solids | |
| 51,93 | g CLP NT042 | |
| 1,70 % | conc. CLP NT042 | |
| 0,88281 | g CLP solids | |
| 0,980946 | g total solids | |
| 90,00 % | CLP:PDAC/(CLP:PDAC + CLP) | |

| Sample | Mass, foil(g) | Mass, glue+foil (g) | Mass, glue+foil dry (g) | Solids content (%) | ABES (N) | |
|---|---|---|---|---|---|---|
| NT057P | 0,596 | 0,69 | 0,629 | 35,11 % | 349,962 | |
| NT050P | 0,8 | 0,834 | 0,812 | 35,29 % | 347,494 | |
| NT058P | 0,584 | 0,702 | 0,627 | 36,44 % | 349,524 | |
| NT051P | 0,49 | 0,539 | 0,508 | 36,73 % | 360,036 | |
| NT049P | 0,829 | 0,868 | 0,846 | 43,59 % | 336,112 | |
| NT052P | 0,648 | 0,678 | 0,662 | 46,67 % | 369,234 | |
| NT048P | 0,622 | 0,705 | 0,664 | 50,60 % | 327,346 | |
| NT043P | 0,655 | 0,766 | 0,719 | 57,66 % | 355,51 | |

**APPENDIX 7.** PF:Dirty Lignoboost adhesives.

| **NT044** | | | |
|---|---|---|---|
| Code | Substance | Quantity | Unit |
| KL955 | Dirty Lignoboost | 0,34 | g |
| PF140J25 | PF | 0,08 | g |
| | | | |
| **NT045** | | | |
| Code | Substance | Quantity | Unit |
| KL955 | Dirty Lignoboost | 0,31 | g |
| PF140J25 | PF | 0,21 | g |
| | | | |
| **NT046** | | | |
| Code | Substance | Quantity | Unit |
| KL955 | Dirty Lignoboost | 0,42 | g |
| PF140J25 | PF | 0,64 | g |
| | | | |
| **NT047** | | | |
| Code | Substance | Quantity | Unit |
| KL955 | Dirty Lignoboost | 0,17 | g |
| PF140J25 | PF | 0,68 | g |